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Semiannual Report Covering the Period April 1985-September 1985

Prepared by P. Soo, Ed.

Brookhaven National Laboratory

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REVIEW OF WASTE PACKAGE VERIFICATION TESTS

SEMIANNUAL REPORT COVERING THE PERIOD APRIL 1985 - SEPTEMBER 1985.

P. Soo, Editor

CONTRIBUTORS

T. Abraham
C. Anderson
E. Gause
H. Jain
P. Soo
T. Sullivan

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Prepared by the Nuclear Waste Management Division
Department of Nuclear Energy
Brookhaven National Laboratory
Upton, New York 11973

Prepared for
Division of Waste Management
Office of Nuclear Material Safety and Safeguards
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555
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ABSTRACT

Several studies were completed this period to evaluate experimental and analytical methodologies being used in the DOE waste package program. The first involves a determination of the relevance of the test conditions being used by DOE to characterize waste package component behavior in a salt repository system. Another study focuses on the testing conditions and procedures used to measure radionuclide solubility and colloid formation in repository groundwaters. An attempt was also made to evaluate the adequacy of selected waste package performance codes. However, the latter work was limited by an inability to obtain several codes from DOE. Nevertheless, it was possible to comment briefly on the structures and intents of the codes based on publications in the open literature. The final study involved an experimental program to determine the likelihood of stress-corrosion cracking of austenitic stainless steels and Incoloy 825 in simulated tuff repository environments. Tests for six-month exposure periods in water and air-steam conditions are described.

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EXECUTIVE SUMMARY

During this reporting period efforts were focused on reviewing several aspects of the DOE program which are concerned with evaluating the performance of the waste package system. In this area, the DOE work is directed at developing tests to produce both relevant performance assessment data and computer codes which will permit a demonstration of compliance with NRC performance criteria given in Final Rule 10 CFR 60.

The specific studies undertaken by BNL over the last six months include:

a) a review of in situ and laboratory measurement made by DOE to accurately characterize the waste package environment in a salt repository,

b) a review of available DOE and related programs on the establishment of radionuclide solubility limits in representative groundwaters,

c) a critique of several DOE performance assessment codes, and

d) an experimental determination of the susceptibility of container candidate materials to stress-corrosion cracking under anticipated tuff repository conditions.

These reviews and evaluations are described below.

Review of In Situ and Laboratory Measurements to Characterize a Salt Repository Environment

The information reviewed in this report has placed emphasis on the characterization of chemical and thermal environments for which there appears to be major uncertainty. The chemical environment includes the composition and volume of brine in the vicinity of a waste package. It was found that additional experimental information is needed to establish the most corrosive brine composition expected in a salt repository. Specifically, the role of magnesium ion needs to be understood. The brines generally used in laboratory tests also do not represent a composition in equilibrium with salt at repository temperatures. Therefore, the composition of the high temperature brine and a method to use it needs to be established. There is very little information available on the effects of the gases associated with salt on the waste package performance, and a detailed characterization of the composition and volume of such gases is needed.

Brine migration rates will become important if container corrosion is assumed to be controlled by the available volume of brine. At present only limited laboratory or in situ information is available on the migration rates of brine inclusions in salt. Rapid migration along the grain or interphase boundaries, and the effect of inclusion size on the migration rate, are the important variables which require extensive investigation.

The thermal environment in salt repository, in principle, can be calculated using analytical codes. However, at present there is an uncertainty in the input values of thermal conductivity which might cause underprediction of the temperatures around a package. In situ data on thermal conductivity as a function of temperature should be obtained to eliminate this source of uncertainty. A verification of analytical codes with in situ temperature profiles, using realistic waste package placement scheme, will help in establishing the confidence in computer predictions.

If the engineered barrier system does not include a self-shielding waste package, gamma and particle radiation will significantly modify the chemical environment. There are indications that gamma radiation may have beneficial effects on the pH of brine, but this speculation is based on very limited data. The effect of radiation on the Eh of brine is also uncertain. There is some information available to identify the stable radiolytic products but very little on highly-reactive transient species.

Gamma radiolysis of brine produces pressures as high as 100 atmospheres. The maximum pressure from alpha radiolysis of brine remains to be determined. A very important additional problem concerns the dissolution of gamma-irradiated salt in brine. The resultant solution pH may range from acidic to highly basic depending on the conditions during radiation.

Radionuclide Solubility Determinations

Radionuclide release rates from a repository will, in certain cases, depend on their solubilities in anticipated repository waters. Based on calculations of inventories at 300 to 1000 years after repository closure, the bulk of the activity in spent fuel or vitrified high level waste is attributable to isotopes of Am, Pu, Np and Tc. The solubilities of these elements and uranium were reviewed in this study.

Depending on the experimental conditions, and the type of specimen (glass or spent fuel) used, there is a wide variation in the solubility data for each element. Most of the studies reviewed approached equilibrium solubility conditions from the undersaturation direction. To obtain reliable results, equilibrium should be approached from undersaturated as well as oversaturated conditions. Only a few studies included the effect of radiation damage in waste package components and the radiolysis of groundwater which could change the Eh and pH of the solution. This, in turn affects radionuclide solubility and colloid formation. The review on plutonium suggests that the solubility data in deionized water may not be the most conservative. It was also found that the higher the sulfate concentration in solution, the less the plutonium solubility, while the presence of fluoride enhanced Pu solubility. For neptunium, the presence of fluoride ions in the solution did not enhance the solubility. The presence of host rock materials and metallic iron in some of the experiments has also resulted in the formation of radionuclide-bearing pseudocolloids or true colloids. Solubilities of technetium and uranium are greatly affected by Eh; increasing the Eh causes higher solubility. The effect of Eh on Pu and Np solubilities is not well defined based on information in the literature. Americium solubility, however, is little affected by Eh changes.

In summary, the review suggests that there is not enough data on radionuclide solubility and colloid formation under anticipated repository conditions and there is a very wide variability in published solubilities caused by differences in redox conditions, groundwater chemistry, and type of specimen used. To obtain conservative estimates of radionuclide solubility and colloid formation in anticipated repository waters, more appropriate experiments should be conducted under conditions simulating the various repository environments.

Evaluation of Selected Performance Assessment Codes

Code and model evaluation conducted during this period have focused on three computer codes used in waste package performance assessment: WAPPA a waste package systems code, BRINEMIG a code that predicts brine migration due to thermal gradients, and TEMP a code that predicts the three dimensional temperature field in a repository.

Review of WAPPA focused on quality control and applicability of using WAPPA in licensing calculations. Quality control on WAPPA was judged through comparing a version of WAPPA released to BNL and updated by letter and a supposedly similar version released to NRC. The comparison found several differences in executing statements indicating a need for better quality control. Letter form updates were singled out as a particularly error prone method for transmitting changes to a code.

Current DOE performance assessment plans for the waste package rely heavily on the WAPPA code. Thus, it must be shown that WAPPA is capable of accurately and reliably calculating the results for the class of problems for which it will be used. However, before developing a procedure to review a single code it was felt a general framework for assessing the usefulness of any computer code in performance assessment should be developed. This framework acknowledges the fact that performance assessment will require the use of a number of process specific codes in conjunction with each other and took the position that review of any code should be done in terms of its specified use in the overall assessment plan.

The current review, based on a WAPPA evaluation, indicates that a viable plan could be based on the following points:

- NRC should require a failure modes and effects analysis to identify all reasonable failure modes.
- The type of code analysis (screening, sensitivity, probabilistic, deterministic) needs to be specified.
- The computer code and documentation need to be reviewed for technical content.

- The usage of the computer code in the failure mode analysis needs to be reviewed.

- The code must be shown to be reliable and accurate, through verification and validation.

- A computer code quality assurance plan needs to be enforced to enable any reviewer to follow the code history.

A brief review of the TEMP code was performed. The analytic nature of the solution procedure offers the advantages of computational speed and ease of use, over traditional finite difference methods. However, the assumption of a homogeneous, isotropic medium with constant thermal diffusivity may limit accuracy in the very near field (i.e. waste package region). TEMP was used in the DOE Environmental Assessment reports to provide the very near field temperature required by other codes in the analysis. Before accepting this procedure, verification of TEMP through comparison with detailed numerical codes on complicated test problems that simulate the repository geometry and environment are necessary.

A short review of the BRINEMIG code was also performed. Due to lack of understanding of migration rates along grain boundaries and lack of data on intracrystalline migration rates, a mechanistic view of brine migration cannot be developed at this time. BRINEMIG attempts to circumvent this problem by using an empirical correlation which gives the maximum migration velocity. Because of the uncertainty involved in modeling brine migration, and in the assumptions made to derive the correlation, a thorough peer review of BRINEMIG is needed.

Below are listed additional recommendations with respect to performance assessment modeling:

- NRC should encourage DOE to enforce a quality assurance plan for computer software used to support HLW repository licensing decisions. Recently DOE has begun to do this, but the results of their efforts are, as yet, unknown.

- Letter form updates for codes should be accepted only as a last resort. All modifications to a code should be transmitted through a quality controlled tape.

- NRC should develop a plan by which codes can be reviewed in terms of their use in the performance assessment plan.

- NRC should vigorously attempt to obtain the computer codes planned for use in the performance assessment in order to enhance detailed reviews of these codes. A significant amount of knowledge was gained by actual use of WAPPA. Up to this time, DOE has been uncooperative in releasing codes in a timely manner.

Stainless Steel and Incoloy-825 Stress-Corrosion Tests

The stress corrosion cracking susceptibility of Types 304L, 316L and 321 stainless steels, and Incoloy 825 is being investigated under simulated tuff repository conditions. Triplicate C-ring specimens of these alloys were exposed to both boiling synthetic J-13 and ten-times-concentrated J-13 water in the presence of crushed tuff, and also the steam phase above these solutions. The test durations are 3, 6, and 12 months. The examination of specimens after the 3-month tests shows that no macroscopic cracking has occurred; the surfaces of specimens tested in steam showed patches of rust and surfaces of specimens tested in the solution had a thin layer of salt and corrosion products. The 6-month tests have been recently completed. A preliminary exmaination of the 6-month test specimens shows similar behavior to the 3-month test specimens, but one Type 316 stainless steel exposed to the steam phase displays what appears to be a crack nucleus.

A comparison of the chemical analysis of solutions at the end of 3- and 6-month tests suggests that some of the species are present as colloids which grow in size with time. An exploratory test to determine the possible range of compositions of repository groundwater suggests that the crushed tuff contains highly soluble salts which include Na^+, K^+, Ca^{2+}, Cl^-, F^- and NO_3^- ions. The solubility of sulphates and silica appears to be controlled, at least in part, by the presence of other ions in the solution.

1. INTRODUCTION

In the licensing procedure for a high level waste geologic repository two NRC criteria are of major importance with respect to the performance objectives for the engineered barrier system. These are detailed in Final Rule 10 CFR 60 (Disposal of High-Level Wastes in Geologic Repositories, Technical Criteria) dated June 1983. The first objective specifies that:

"Containment of HLW within the waste packages will be substantially complete for a period to be determined by the Commission taking into account the factors specified in subsection 60.113(b) (of 10 CFR 60) provided, that such period shall be not less than 300 years nor more than 1,000 years after permanent closure of the geologic repository"; and the second states that:

"The release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission; provided, that this requirement does not apply to any radionuclide which is released at a rate less than 0.1% of the calculated total release rate limit. The calculated total release rate limit shall be taken to be one part in 100,000 per year of the inventory of radioactive waste, originally emplaced in the underground facility, that remains after 1,000 years of radioactive decay."

The Environmental Protection Agency criteria addresses the release of radionuclides to the accessible environment, in terms of cumulative curies released, that are permissible over a 10,000 year period. These release limits are summarized in Table 1.1.

In order to show compliance with these performance objectives the license applicant will need to provide a data base and analyses to quantify anticipated behavior of the waste package/repository system before and after permanent closure. This will necessarily involve research and testing programs to evaluate the likely modes by which engineered system components will degrade or fail by chemical or mechanical means. Knowledge of the ways in which the engineered barriers fail or degrade will permit estimates to be made regarding the containment capability of the waste package and the radionuclide release rate from the engineered barrier system.

An extremely important factor in any research effort to compile a data base for engineered barrier system performance assessment is the quality of the data produced. Information obtained under non-prototypic conditions will lead to uncertainty when performance assessment calculations are made. This could lead to an overall inability to show that regulatory criteria will be met. Clearly, there is a need to estimate waste package/repository conditions, including those for the preclosure period, for extended periods of time. Once these are known, experiments may be designed to incorporate these conditions so that defensible performance data may be acquired. Tables 1.2 through 1.4 give estimates of waste package/ repository conditions (NUREG/CR-2482, Vol. 7, 1984). The values were obtained from information in the literature but they should be regarded as tentative since parameters such as temperature, radiation levels, groundwater flow rates, etc., may change as waste package designs become finalized and as site characterization studies mature.

Table 1.1 Acceptable cumulative releases to the accessible environment for 10^4 years after disposal as specified in proposed 40 CFR 191.

Radionuclide	Release Limit Ci/1000 MTHM
^{241}Am	10
^{243}Am	4
^{14}C	200
^{135}Cs	2,000
^{137}Cs	500
^{237}Np	20
^{238}Pu	400
^{239}Pu	100
^{242}Pu	100
^{226}Ra	3
^{90}Sr	80
^{99}Tc	2,000
^{126}Sn	2,000
Other α-emitting radionuclides	10
Other radionuclides (γ, β)	500

The emphasis of the current program is to review test methodologies and computer codes that are being used by the DOE community to generate waste package performance information. A primary goal is to determine whether the tests, codes, and the data are sufficient for licensing purposes. For situations where uncertainty exists, recommendations for future work are specified. In some cases, short-term testing is carried out in the current program to resolve a particular technical problem.

In the sections below several areas have been investigated over the last 6-month period. An attempt has been made to determine the state of knowledge of the environmental conditions to be expected in salt repositories. A second program evaluates the test methodology and data base for radionuclide solubility and radio-colloid formation since these are central in determining the rate of release of radionuclides from the engineered barrier system. Efforts to evaluate selected DOE waste package performance codes are also described. Finally, progress in the stainless steel and Incoloy 825 stress-corrosion

Table 1.2 List of estimated spent fuel waste package conditions for a salt repository.

Parameter	Estimated Value			
	Operations Period	Thermal Period (0-300 yr)	Transition Period (300-1000 yr)	Geologic Control (>1000 yr)
Temperature at Centerline (Thermal Loading 12.4 W/m^2)		375°C max.	Approximately 150-110°C	<110°C
Total Gamma Dose (rad)		10^9-10^{10}	Little additional irradiation.	Little additional irradiation.
Brine Flow Rate (Thermal loading 12.4 W/m^2)		Total of about 3 liters per borehole.	Little additional brine inflow	Little additional brine inflow
Brine Chemistry	Brine A or Brine B chemistries depending on repository location.	Brine A or Brine B with significant NaOH levels.	Brine A or Brine B with NaOH present.	
pH (measured at 25°C)	Steam/air plus small amounts of $HCl/SO_2/CO_2/H_2S$.	Initially acidic brine (pH =3.5) due to dissolution of acid gases. Changing to alkaline brine because of dissolution of colloidal sodium by brine inclusions. pH could rise to 9.5 based on experiments with irradiated salt and deionized water.	Probably alkaline.	Probably alkaline.
pH (at high temperature)		Lower than values measured at 25°C but no reliable values can be specified because of complex hydrothermal reactions and irradiation effects.		
Redox Conditions	Oxic	Probably oxic due to brine radiolysis.	Approaching anoxic	Probably anoxic.
Stress (MPa)	0.1	Initially 0.1 MPa, rising to lithostatic stress of 16.2 MPa as host rock settles.		

Table 1.3 List of estimated spent fuel waste package conditions for a basalt repository.

Parameter	Estimated Value			
	Operations Period	Thermal Period (0-300 yr)	Transition Period (300-1000 yr)	Geologic Control (>1000 yr)
Temperature at Centerline (Thermal Loading 13.0 W/m^2)	250°C	265°C max. after ≈35 yr.	140-125°C	<125°C
Total Gamma Dose (rad)		10^7-10^8	Little additional irradiation.	No additional irradiation.
Vertical Hydraulic Conductivity (m/sec.)		Unknown, but likely to be much greater than that for horizontal flow because of buoyancy effects.		
Water Chemistry	Steam/air	Significant increases in K^+, Ca^{2+}, Fe, Si, and SO_4^{-2} in the packing material water at higher temperatures. F^- is reduced in concentration.		Not known, but there should be a tendency to return to original Grande Ronde water chemistry.
pH (measured at 25°C)		Initially 8.0 in packing material water, decreasing to 6.5-7.5.	Increasing to approximately 9.0.	
pH (at high temperatures)		Lower than values measured at 25°C but no reliable values can be specified because of complex hydrothermal reactions and irradiation effects.		
Redox Conditions	Oxic.	Probably oxic due to water radiolysis.	Approaching anoxic.	Possibly anoxic.
Stress (MPa)	0.1	Initially 0.1 MPa, rising to a value between hydrostatic and lithostatic stresses (11 to 33 MPa).		

Table 1.4 List of estimated spent fuel waste package conditions for a tuff repository.

Parameter	Estimated Value			
	Operations Period	Thermal Period (0-300 yr)	Transition Period (300-1000 yr)	Geologic Control (>1000 yr)
Temperature at Centerline* (Thermal Loading 12.4 W/m^2)		330°C max. to 100°C	100-60°C	<60°C
Total Gamma Dose (rad)		$\approx 10^{10}$	Little additional irradiation.	No additional irradiation.
Water Flow Rate	Steam/air conditions.	Steam/air for first several hundred years followed by liquid water flowing at < 1 mm/yr.	< 1 mm/yr.	< 1 mm/yr.
Water Chemistry	Steam/air conditions.	Probably similar to J-13 well water after steam conditions subside. May be more concentrated than J-13 water if precipitated salts redissolve.	Probably similar to J-13 well water but could be more concentrated if precipitated salts redissolve.	
pH (Measured at 25°C)		7.1 for J-13 well water. May be acidic because of radiolysis of $N_2/O_2/H_2O$ mixtures.	≈7.1	≈7.1
Redox Conditions	Oxic	Oxic	Oxic	Oxic
Stress (MPa)	0.1	Initially 0.1 MPa, rising to the lithostatic stress of 8.6 MPa as host rock settles.		

*Calculations were made for waste package without packing material.

cracking program are given. This testing effort was designed to determine whether candidate container materials are susceptible to stress-induced failure in anticipated tuff repository environments.

1.1 Reference

NUREG/CR-2482, Vol. 7, BNL-NUREG-51494, "Review of DOE Waste Package Program - Subtask 1.1 National Waste Package Program, Biannual Report," E. Gause and P. Soo, Brookhaven National Laboratory, September 1984.

2. REVIEW OF IN SITU AND LABORATORY MEASUREMENTS TO CHARACTERIZE THE SALT REPOSITORY ENVIRONMENT

2.1 Introduction

For the disposal of high level nuclear waste (HLW), NRC requires that the waste must be substantially contained within the waste package for a period of 300-1000 years from the time of repository closure. Clearly, the containment period will be determined by the environmental conditions to which the package will be exposed. Among these, geochemistry of the host rock, groundwater characteristics, temperature, radiation levels, and pressure are the most important parameters which must be known with sufficient certainty to predict container life time. Once the range of parameters is established, experiments in the laboratory can be conducted on appropriate test materials under meaningful conditions, and the resulting data may be used in predicting the waste package performance.

A determination of the chemical and thermal environments requires more extensive testing than for the radiation or pressure environments since these can be calculated with less uncertainty. Nevertheless, radiation and pressure can significantly affect the overall characteristics of a repository and, therefore, should be included in interactive tests. At present, the range of experimental conditions, used in various laboratories, and presumed to represent anticipated repository conditions, is mostly based on indirect calculations, limited laboratory and in situ measurements, or data collected for locations not under consideration for a repository. The lack of information is also, in part, because the design of the engineered barrier system has not been finalized and, therefore, interactive effects among various components are not known. To evaluate the extent and source of uncertainty in the ranges of repository conditions, pertinent DOE, NRC and foreign work on salt host rock is reviewed here with emphasis on information which:

a) involves water sampling at depth and determination of its chemical composition, pH and Eh,

b) involves laboratory water/rock interactions at high temperatures to examine the parameters specified in (a) above,

c) involves in situ tests in which the repository environment is quantified.

An important part of this study is to identify those tests on the waste package system which are conducted under non-prototypic conditions. This would make much of the data obtained of little technical value.

There are seven prospective sites being considered by the Department of Energy for the permanent disposal of HLW in salt formations. These are:

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a) Richton Dome Site, Perry County, Mississippi
b) Vacherie Dome Site, Webster and Bienville Parishes, Louisiana
c) Cypress Creek Dome Site, Perry County, Mississippi
d) Lavender Canyon Site, Paradox Basin, San Juan County, Utah
e) Davis Canyon Site, Paradox Basin, San Juan County, Utah
f) Deaf Smith County Site, Palo Duro Basin (Permian), Texas
g) Swisher County Site, Palo Duro Basin (Permian), Texas

The characteristics of salt deposits at these sites can be divided into two categories, viz., domal (first three sites) or bedded (last four sites) depending on how the salt was formed. On the average, bedded salt is believed to contain a ten times larger volume of brine inclusions than domal salt. There are also differences in the characteristics of salts from the Paradox and Palo Duro (Permian) Basins. For example, significant amounts of carnallite and kieserite minerals are found in the Paradox Basin salt, but not in the Palo Duro Basin salt. Thus, some of the characteristics of a salt repository are likely to be site-specific. Recently, site-specific information was generated by several investigators (see, for example, BMI/ONWI-522, 1983; Versluis, W.S., 1984; Hubbard, N., 1984; Pederson, L.R., 1984), which may be used in redefining the repository conditions for use in waste package, corrosion, and leach tests in the laboratory. However, it should be noted that such information has been mostly obtained from laboratory tests which may not always represent in situ conditions. In the following sections, testing methods and available information defining chemical and thermal environment in a salt repository are reviewed. The effects of irradiation in altering the repository conditions are finally considered.

2.2 Chemical Environment

A salt formation usually contains inclusions or cavities of brine solution. Under the thermal gradient produced by a HLW package, salt at the hot side of an inclusion will dissolve, and precipitate on the cooler side. This effective migration of brine to, and its subsequent accumulation at, the hot container surface is perhaps the most detrimental factor for container integrity because of the corrosive nature of brine. Chemical composition as well as volume of brine would determine the type and extent of corrosion which would breach the container. Therefore, it is important to know the limiting values of these parameters which should be used in laboratory testing or analytical modeling.

2.2.1 Range of Brine Compositions

Since a brine is expected to be in equilibrium with the surrounding rock salt, its composition can be expected to have as wide a range as of the salt mineralogy itself. Because of this it is not possible to identify a unique brine composition which would represent all repositories. Molecke (SAND 83-0516, 1983) has listed ionic compositions of 18 brines used by different workers. These are divided into two categories as given in Tables 2.1 and 2.2, respectively, depending on the concentration of magnesium ions. The brine A-like category has at least one order of magnitude higher magnesium concentration than the brine B-like category. Experimental data on uniform

Table 2.1 Brine "B-like" brine composition comparisons mg/L (SAND 83-0516, 1983).

Ion	(WIPP/ Generic) Brine B (±3%)	ONWI Composite Permian P	Equilibrated Permian P no. 2	Pretest PNL-SNL	Brine-Backfill PNL-SNL	Posttest PNL-SNL	Flow WIPP-12	Downhole WIPP-12	Flow ERDA-6	Downhole ERDA-6
Na^+	115,000	123,460	123,000	159,000	155,000	119,000	114,000	140,000	112,000	140,000
K^+	15	39	39	2,550	2,370	5,000	3,100	3,200	3,800	4,800
Mg^{++}	10	134	122	409	463	158	1,700	1,400	450	270
Ca^{++}	900	1,560	1,100	370	695	267	410	380	490	360
Sr^{++}	15	35	35	18	43	34	15	--	18	--
Zn^{++}		7.8	8	< 2.5	--	199	0.5	--	0.6	--
Li^+	20						220	210	240	205
Rb^+	20									
Cs^+	1			--	--	64				
Fe^{+++}	2			< 5	--	55	3.6	6.3	3.6	5.7
Cl^-	175,000	191,380	191,000	190,000	231,000	197,000	160,000	180,000	170,000	180,000
SO_4^{--}	3,500	3,197	1,910	2,086	3,237	16,300	17,000	18,000	16,000	14,000
B(as BO_3^{---})	1,200			16	11	1,280	1,200*	960*	680*	740*
HCO_3^-	700	38	23	7.8	15	0	2,600	2,400	2,600	1,800
Br^-	400	32	24				430	460	880	720
I^-	10									
F^-		1.1	1.0	37	37	0	4.3	--	1.7	--
pH:	6.5	7.055		6.9	6.8	3.8	7.17	7.76	6.42	7.02
Field Eh: (mV)							-211		-152	

---

*Values reported as B, but assumed to actually be BO_3^{---}

-- = below measureable detection limits

Table 2.2 Brine "A-like" and other brine composition comparisons mg/L (SAND 83-0516, 1983).

							OTHER		
Ion	(WIPP/ Generic) Brine A (±3%)	WIPP Inclusion No.1 (Preliminary)	WIPP Inclusion No.2 (Preliminary)	MCC Brine	Quinare Brine Q (±10%) (55°C)	USGS MBT-6a (±10%)	Saturated NaCl (20°C)	Saturated NaCl (100°C)	Seawater
Na^+	42,000	63,000 ± 5000	32,000 ± 1,100	35,400	6,500	27,000	142,000	154,000	10,651
K^+	30,000	8700 ± 500	6800 ± 200	25,300	29,000	35,000			380
Mg^{++}	35,000	23,000 ± 2000	40,000 ± 1400	29,600	85,000	33,000			1,272
Ca^{++}	600	210 ± 20	150 ± 10			47,000			400
Sr^{++}	5								13
Zn^{++}									
Li^+	20								
Rb^+	20								
Cs^+	1								
Fe^{+++}	2								
Cl^-	190,000	160,000 ± 9,000	160,000 ± 5000	164,000	270,000	250,000	218,000	237,000	18,980
SO_4^{--}	3,500	13,200 ± 2600	13,200 ± 2600		13,000				884
B(as BO_3^{---})	1,200								
HCO_3^-	700								146
Br^-	400								65
I^-	10								0.05
F^-									
pH:	6.5			6.5					8.1

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corrosion of various alloys have consistently shown Brine A to be more corrosive than Brine B or seawater. Based on this observation corrosivity of Brine A has been attributed to a decrease in the pH when magnesium oxysulfates are precipitated or when $MgCl_2$ in brine reacts with SiO_2 (from the waste form or packing material). According to Molecke, (1983):

$$3MgCl_2 + 4SiO_2 + 4H_2O = Mg_3Si_4O_{10}(OH)_2 + 6H^+ + 6Cl^-.$$

That is, the decrease in pH and hence the corrosivity of brine increases with increasing magnesium concentration. However, there is no detailed study to show that the concentration of Mg^{++} is the only major factor an the corrosivity of a brine or what is the imporance of possible interactions between brine and other waste package components.

Hubbard an others (1984) have listed compositions of brines (Table 2.3) which represent inclusions in Cycle 4 of the Permian Lower San Andres Formation at the Deaf Smith Site. Pederson and others (1984b), in addition, give the composition of a brine from Paradox Basin (Table 2.4). They note that this brine contained a relatively high concentration of H_2S ($S^{--} > 37$ ppm) - a corrosive constituent which is not included in commonly-used Brine A or Brine B.

Table 2.3 Palo Duro brine compositions compared with WIPP brine compositions (mg/L). (Hubbard, N., 1984)

	Fluid(1) Inclusions		Fluid(2) Inclusions	(3) Dissolution Brine-	Recommended Fluid Inclusion	Dessication Brine (5)	WIPP Brine (3)			
	#1A	#1B	#2	PNL	Brine(4)	($MgCl_2$ Brine)	Brine B Dissolution	Brine A	Fluid Inclusions (preliminary)	
Ca^{++}	---	---	12,630	1,560	1,336	---	900	600	210	150
Mg^{++}	50,000	50,500	18,810	134	50,000	138,720	10	35,000	23,000	40,000
Na^+	49,000	55,200	78,840	123,460	25,290	---	115,000	42,000	63,000	32,000
K^+	15,690	15,800	5,030	39	15,690	---	15	30,000	8,700	6,800
$SO_4^=$	61,450	76,200	470	3,197	3,200	---	3,500	3,500	13,200	13,200
Cl^-	191,000	187,900	200,900	191,380	200,000	406,260	175,000	190,000	160,000	160,000

(1) Brine 1A has the centroid Mg value from Figure 5, with the concentrations of other ions estimated from simple evaporation of seawater.
Brine 1B is an observed composition reported in Carpenter [9] for simple evaporation of sea water.

(2) This is an observed brine in a modern carbonate sabkha, Trucial Coast, Persian Gulf [13]. This brine has extensively participated in dolomitization.

(3) Data from [14].

(4) This has the centroid Mg value from Figure 5, with the Ca^{++} and $SO_4^=$ values taken to be the saturation values at molar $Ca^{++}/SO_4^= = 1.00$. Molar $Ca^{++}/SO_4^=$ ratios different from one is perhaps more likely but not important because of the effectively unlimited supply of anhydrite to saturate the brine.

(5) This is an extreme brine composition that could result from extensive dessication of a high-Mg brine. The Mg^{++} and Cl^- concentrations given are for a saturated solution of $MnCl_2$. See Jenks [16] for a detailed explanation of how such brines could form.

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Table 2.4 Compositions of saturated salt brines from various potential nuclear waste sites, 25°C. (Pederson, L.R., 1984b)

Ion	Permian Basin+ Cycle 5	Permian Basin++ Cycle 4	Permian B. Cycle 4 150°C	Paradox Basin* Cycle 6	WIPP A**	WIPP B**
Na^+	114,100***	127,000±300	123,000	121,400	42,000	115,000
K^+	45	40±2	39	670	30,000	15
Ca^{2+}	1,460	1,580±40	1,100	820	600	900
Mg^{2+}	104	132±23	122	750	35,000	10
Sr^{2+}	52	34±1	35	31	5	15
Zn^{2+}	8	8±2	8			
Cl^-	185,000	191,300±600	191,000	181,300	190,000	175,000
SO_4^{2-}	3,700	3,260±100	1,910	3,500	3,500	3,500
HCO_3^-	30	28±15	23	47	700	700
Br^-	30	27±6	24		400	400
BO_3^{3-}	<10	<10	<10	<10	1,200	1,200
S^{2-}					≥37	

+Zeeck Core Hole No. 1, Lower San Andres
++G. Friemel Core Hole No. 1, Lower San Andres
*GD-1, Gibson Dome
**Reference 1
***ppm by weight

Considering the large variability in brine compositions, investigators have suggested the use of "limiting compositions" corresponding to two scenarios of brine migration to the waste package. In the first case, external water enters and floods the repository to form "dissolution brine." This is expected to have a composition similar to Brine B described in Table 2.1. In the second case, existing brine inclusions migrate to the waste package due to the presence of a thermal gradient. Molecke (SAND 83-0516, 1983) has suggested that the composition of these brine inclusions will be similar to that of Brine A (Table 2.2). That the inclusion brines have a higher Mg^{++} concentration than the dissolution brine is a general observation. Exceptions to this observation are possible if the salt contains higher than normal magnesium compounds. Typically the bedded salt contains higher amounts of impurities and, therefore, it is not surprising to find unusually high magnesium levels in the brine prepared by dissolving salt from the Utah site. It is logical to believe that the composition of inclusion brine at this site may also be higher in magnesium than a similar brine at a domal site. It is because of variation in the salt compositions at different sites, that site-specific brine compositions need to be determined.

Both Brine A and Brine B are based on the samples taken from the vicinity of WIPP site which is located in southeastern New Mexico. This site is in the Delaware Basin which is a portion of the larger Permian Basin. Brine B presumably represents a near saturated solution of salt at domal sites or relatively pure bedded halite. It is based on an analysis of the brine obtained by equilibrating rock salt with deionized water at 100°C, cooling the solution to equilibrate at room temperature and then filtering out the insolubles. Brine A is based on the chemical analysis of the fluid found in inclusions at WIPP site. Compositions for two inclusions are included in Table 2.2. After discussing the composition of various brines, Molecke (SAND-83-0516, 1983) recommends the use of Brine A in container corrosion studies and barrier material interaction testing. Brine B or site specific Permian Brine P is recommended for use in waste form leaching experiments. It is important to note that the inclusions at the WIPP site also contained up to 70 vol% of a gaseous phase. The MCC Brine in Table 2.2 is a simplified version of Brine A, which would not show any precipitation on heating to 90°C. Brine Q which is used in laboratory testing in West Germany is very rich in magnesium and more representative of a site in that country than in the United States.

Hubbard and others (1984) consider that the inclusions, for example, in the Palo Duro Basin were produced at the time when salt was formed from the evaporation of seawater. By considering the onset of crystallization of Na, K and Mg minerals from the evaporation of seawater as a function of magnesium content in solution, they suggest a range of possible and expected magnesium concentration in inclusions as shown in Figure 2.1. The brine in such inclusions has a much higher magnesium concentration (Table 2.3, #1A and 1B) and is, therefore, possibly more corrosive than Brine A. Hubbard and others (1984) further point out that evaporation of brine inclusions can produce an almost pure $MgCl_2$ "dessication brine." However, their recommended fluid inclusion brine is similar to seawater evaporated brine but with much smaller SO_4^{--} concentrations. At present, corrosivity of these brines with respect to Brine A is not known. Considering the wide use of Brine A in laboratory corrosion tests, it is imperative to determine its corrosivity with respect to the brines of "limiting compositions," described above.

2.2.1.1 Effect of Temperature on Brine Composition

All of the brine compositions mentioned above represent ionic concentrations measured on solutions at room temperature. These solutions were first prepared by equilibration with rock salt at various temperatures followed by filtration at room temperature. The compositions listed in Tables 2.1 through 2.4, therefore, have the advantage of easy handling at room temperature without any precipitation. However, a waste package during the first several hundred years after repository closure will be in contact with brine at high temperatures (up to ≈300°C). The ionic concentrations and also the corrosivity of a brine solution at these temperatures will very likely be much higher than for any of the presently considered brines. For example, at 25°C, Brine A has 25.5 weight percent total dissolved solids (TDS) which increases to 34.0 weight percent at 200°C (Stewart,D.B., 1978). Bitterns near the waste containers may contain 35 to 55 weight percent TDS and values as high as 75 weight percent are possible (Stewart, D.B., 1978).

At high temperatures, not only the weight percent of TDS is much higher than at room temperature, but relative concentrations of various corrosive species as well as pH and Eh are expected to be different. That is, the currently used synthetic brines might be significantly less corrosive than the brines expected in the repository at high temperatures; thus any high temperature tests in brine should be conducted in brine compositions representative of the test temperature. To prepare appropriate "high temperature" brines, the composition of inclusion or intrusion brines needs to be determined at temperature. However, due to complex dependence of solubility equilibria on temperature, it may not be easy to determine the chemistry of brine in inclusions at repository temperatures. In this case, as an approximation to the repository situation, solid salt may be added to the test solution (such as Brine A) so that saturation conditions prevail at the test temperature.

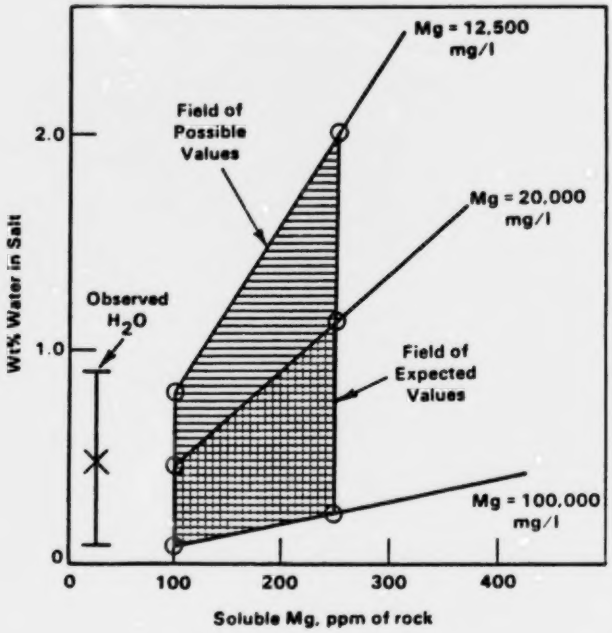


Figure 2.1 Expected content and Mg concentration of fluid inclusions in the Lower San Andres salt beds in depositional Cycle 4. The fields of possible and expected values are derived from a simple model of sea water evaporation. (Hubbard, N., 1984)

2.2.1.2 Effect of Waste Package Components on Brine Composition

Changes in brine chemistry can also arise from interactions with other components in waste packages. Molecke and others (1982) in a PNL-Sandia collaborative work have examined the effect of brine interaction with packing material. A brine prepared from the dissolution of bedded salt from Southeastern New Mexico was mixed with packing made of 30 weight percent smectite clay and 70 weight percent silica sand and heated to 250°C for 95 days. As shown in Table 2.5, the pH of post-test brine changed to 3.8 from the starting value of 6.8, and its SO_4^{--} concentration increased by a factor of five. This post-test brine is likely to be more corrosive than the starting solution. The authors suggested that reaction of $MgCl_2$ with silica and aluminosilicetes resulted in lower pH. It is not clear whether pH could be lowered further if a brine of higher $MgCl_2$ were used in such a study. It should be noted that a lower pH could also be caused by the thermal release of acidic gases from the heated salt (see Section 2.2.2). At present, very little is known about the relative corrosivity of brines in equilibrium with various waste package components at high temperatures. In this regard we note some interesting observations from the preliminary experiments by Westerman and Pitman (PNL-SA-12344, 1984). They found that the corrosion rates of A216 steel are up to 30 times greater in a moist salt environment than those found in an intrusion brine, thus emphasizing the importance of interactive effects of various waste package components. Therefore, it is suggested that some testing be conducted to determine the variation of concentration, pH, corrosivity and leachability of "limiting composition" brines in equilibrium with other components of the waste package under near-field repository conditions.

Table 2.5 Pre- and post-test brine compositions, mg/L.
(Molecke, M.A., 1982)

Element	Pre-Test Brine	Brine & Backfill	Post-Test Brine
Na	159,000	155,000	119,000
K	2550	2370	5000
Ca	370	695	267
Mg	409	463	158
Sr	18	43	34
Cs	N/A	N/A	64
Mo	< 5	<5	24
B	3	2	236
Zn	<2.5	N/A	199
Mn	<0.5	N/A	32
Fe	<5.0	N/A	55
Cr	<0.5	N/A	1.2
Ni	<1.5	N/A	4.3
$SO_4^=$	2086	3237	16300
HCO_3^-	7.8	15.0	0
F^-	37	37	0
Cl^-	190,000	231,000	197,000
U	-	-	0.1
pH	6.9	6.8	3.8

2.2.2 Gases Associated with Salt and Brine

Brine is expected to be the most important factor in breaching a HLW container and leaching the waste form, but the presence of any corrosive gases can also enhance the corrosion process and thereby shorten the containment period. In defining the chemical environment in a salt repository the role of a gaseous phase has been generally neglected. Considering that corrosive gases can be generated by simple heating of salt or radiolysis of brine, there is a need to estimate the composition as well as the effects of such gases. Molecke (SAND 83-0516, 1983) stated that inclusions in salt may contain up to 70 vol% gas. However, the composition of such gases remains to be determined. Claiborne and others (ORNL/TM-7201, 1980) have suggested that inclusions containing a gas phase will move away from the heat source. Indeed, Roedder and Belkin (1980) observed the migration of predominantly gas-filled inclusion down the thermal gradient. They also observed the splitting of gas- and liquid-filled inclusions so that gas inclusions move in a direction opposite to that for the liquid inclusions. Although the data are based on only five gas rich inclusions, they noticed that a gas inclusion moved much faster than the liquid inclusion of the same size (by a factor of 1.25 to 10). The mechanisms for these phenomena are not established and their impact on corrosion is highly complicated in view of the fact that, initially, there will be a significant volume of air present around the waste package, and a salt deposit is not a perfect solid but contains cracks, grain boundaries, cavities, etc. However, at present, it is known that gases such as H_2S, SO_2 and HCl which could be detrimental to metallic containers are produced when salt is heated to high temperatures. Jockwer (1984) and Uerpmann and Jockwer (1982) have found that when salt from the Asse mine in West Germany is heated to 350°C, the following gases are liberated:

CO_2: up to 400 ppm
H_2S: 5 ppm
HCl: 150 ppm
gaseous hydrocarbons: 60 ppm

CO_2, H_2S and hydrocarbons are present in the rock salt, whereas HCl is generated by thermal decomposition of some trace minerals. Elemental sulfur has been found in the caprock just above the salt domes which may be corrosive in solid as well as gaseous form. Thus, the concentration of these gases will strongly depend on the source and composition of a rock salt specimen. In a recently-presented paper, Pederson (1984a) reported the evolution of HCl, SO_2, CO_2 and H_2S on heating Palo Duro and Paradox Basin rock salt to 250°C. The details of this study are yet to be published but it is important to note that HCl was the most prevalent component.

Finally, it is interesting to note that evolution of gases from salt during heating to repository like temperatures may significantly change the characteristics of salt. For example, Panno and Soo (1984) observed evolution of H_2, O_2, CO_2, SO_2 and H_2O when salt samples from Carlsbad, New Mexico were heated slowly to 180°C. The pH of brine prepared by dissolving the heat treated salt depended on annealing temperature. Figure 2.2 shows that pH of brine prepared from as received salt was ≈ 6.5, but when a specimen was

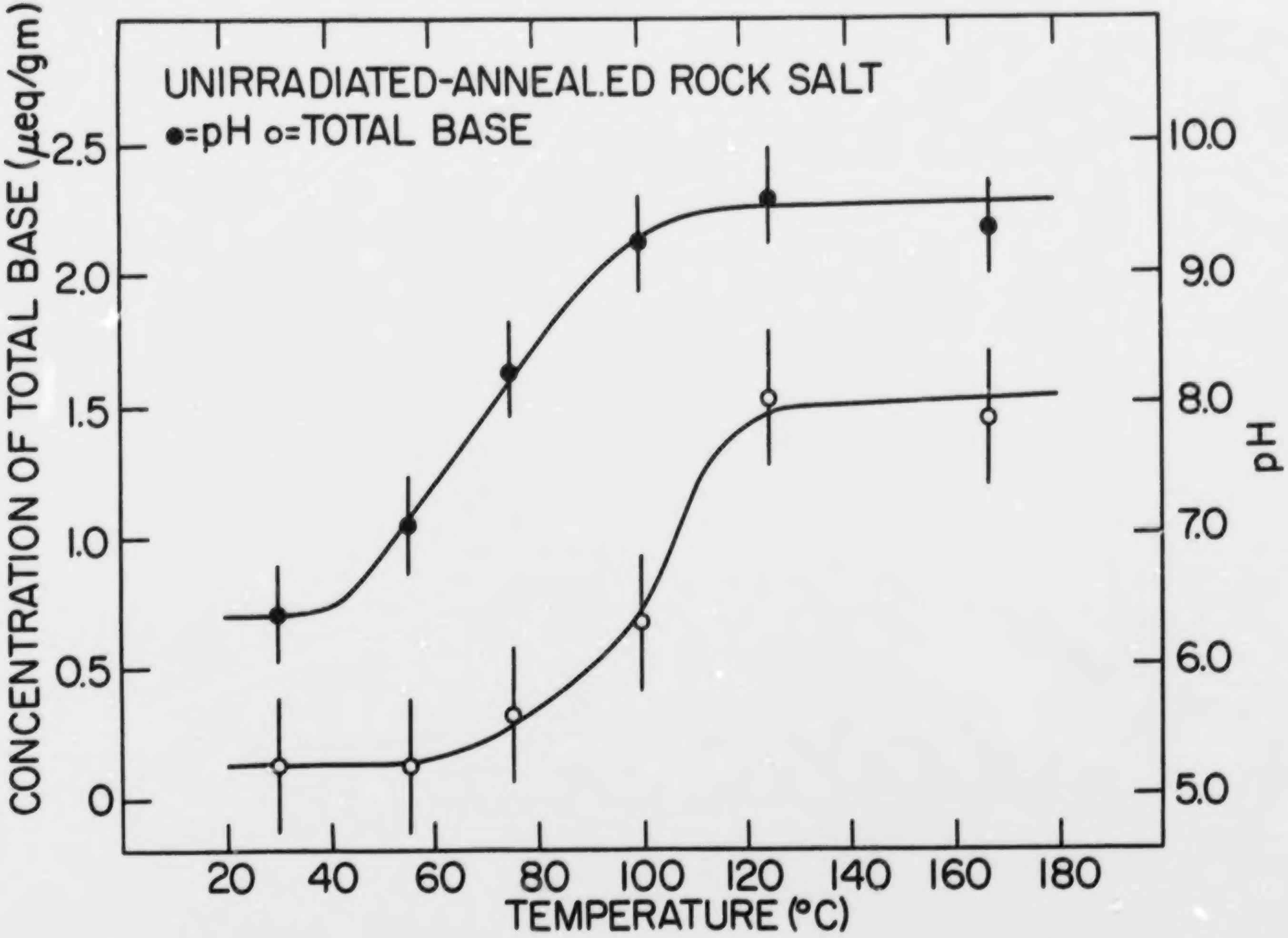


Figure 2.2 Plot of pH and total base of brine vs temperature of annealing of parent rock salt showing the temperature sensitivity of the rock salt. (Panno, S.V., 1984)

annealed at 125°C for 24 hours and then dissolved, the pH of solution increased to 9.5. The authors suggest that the increase in brine pH is due to the loss of acidic gases during heating.

2.2.3 Brine Volume

Most of the laboratory corrosion and leaching tests are being conducted in significant volumes of brine so that corrosion and leaching data are not limited by its availability. However, in computer modeling of waste package behavior, some authors (Jansen, G., 1984) have suggested that corrosion of the container would be limited by the availability of brine. If such an assumption is appropriate, total brine accumulation at the waste package becomes a critical parameter in predicting the container lifetime.

2.2.3.1 Experimental Studies of Brine Migration

At present, there are no in situ data which give the volume of brine accumulation at a prototypic waste package surface. However, a few experiments have been carried out to estimate thermally-induced brine accumulation from the rate of brine migration in salt from different locations.

Some of the initial laboratory information on brine migration is from experiments conducted under Project Salt Vault (ORNL-4555, 1971). In this work brine migration rates were determined for 1 inch cube salt specimens from Hutchinson, Kansas, containing brine inclusions of 2-10 mm size. Temperature gradients ranging from 4 to 34°C/cm were applied at 75 to 244°C. Brine migration rates were found to be in the range of mm/day for temperatures higher than 100°C. The results are shown in Figure 2.3, where the solid line is based on theoretical calculations using a diffusion model. Note that the data have a large scatter, particularly at high temperatures. Total inflow of 2 to 10 liters brine was calculated per waste container, taking place over 20-30 years. These results are very approximate and more careful experiments under better controlled and larger ranges of conditions would be desirable if the brine accumulation volume is to be treated as the corrosion-limiting parameter.

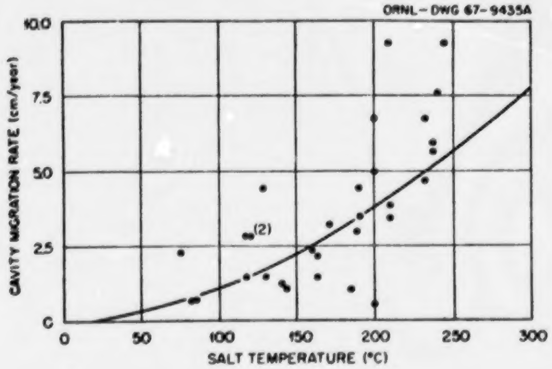


Figure 2.3 Comparison of theoretical and experimental migration rates of brine-filled cavities in rock salt. (ORNL-4555, 1971)

Recently, Roedder and Belkin (1980) measured the migration rate of brine inclusions in salt specimens from the WIPP site under a thermal gradient of 1.5°C/cm. Some scoping experiments were also conducted on salt from Vacherie Dome, Louisiana. The migration rates in these experiments were much slower than obtained on samples in Project Salt Vault (Bradshaw, R. L., 1969), presumably due to the larger size of the inclusions in the latter work. That is, inclusion volume seems to be an important parameter in determining the migration rate, as shown in Figure 2.4. It is, perhaps, for this reason that Roedder and Belkin (1980) found much smaller migration rates in domal salt specimens. For bedded salt repositories, these authors note that the bulk of the water is probably present in inclusions larger than used in their study (>> 1 mm) and, therefore, their results represent the lower limit of brine influx into a borehole. An important conclusion from this study is that the migration rates could vary as much as a factor of 3 even within the same rock salt core. The authors conclude "... it would be hazardous to extrapolate these rates to a calculation of expected brine flow in a given storage scenario." Clearly, there is a need for further experiments on site-specific samples in the maximum anticipated thermal gradient.

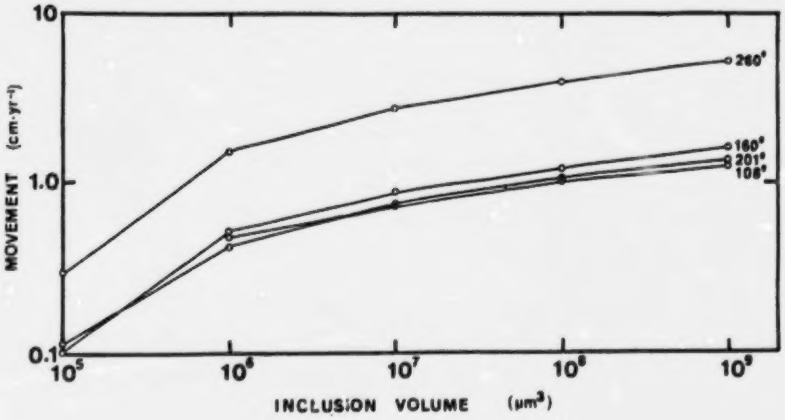


Figure 2.4 Migration rates of various sizes of fluid inclusions in salt sample 2061, after 72-252 hours at 1.5°C cm^{-1} gradient and the ambient temperatures indicated. Each curve is based on smoothed data for a group (17 to 44) of inclusions. (Roedder, E., 1980)

An attempt has been made at the Avery Island salt mine near New Iberia, Louisiana, to estimate the in situ brine migration rates in domal salt (ONWI-190(4), 1983). At this site three tests were carried out to measure (a) natural brine movement under ambient temperature (AB), (b) natural brine movement under elevated temperature (NB), and (c) synthetic brine movement under elevated temperature conditions (SB). In these tests the maximum salt temperature was 51°C, which is much lower than the expected repository temperature. The brine accumulation, determined from the moisture collected in corresponding bore holes, is shown in Figure 2.5 as a function of time. Note that for the case of synthetic brine, the moisture collected increased sharply during cooling. This increase has been attributed to the microcracking and opening of grain boundaries. Krause (ONWI-190(4), 1983) analyzed the steady state brine flow data from these experiments in terms of the model developed by Anthony and Cline (1971) for single crystal salt. He suggested that the agreement between the experimental results and the model is very good. However, for the following reasons this apparent agreement may be partly coincidental, and the model would have limited applicability to the complete range of repository conditions: (a) The salt in a repository is polycrystalline, and the model does not consider rapid migration of brine along the grain boundaries (see below). (b) The effect of inclusion size on brine migration has been generally observed, but not considered in the model. (c) In spite of a large uncertainty in the input parameters, the agreement between the model and the data is very good. (d) Contrary to intuition, the moisture collection was smaller when additional synthetic brine was present in the heated zone than when only natural brine was present.

The results from experiments currently in progress at the Asse mine in Federal Republic of Germany (Figure 2.6) are expected to produce some in situ data (BMI/ONWI-539, 1984). In these experiments brine, which migrates to boreholes (at a maximum temperature ≈ 210°C) under a temperature gradient of 3°C/cm, is continuously collected (as moisture) under atmospheric conditions or allowed to accumulate under enclosed hydrothermal conditions. In two boreholes ^{60}Co radiation sources were also included to simulate an actual waste package. Results from this program reported to date suggest that brine collection in the borehole open to atmospheric conditions is approximately 77 cc after 219 days of operation, which is a factor of 2 higher than in the closed borehole. These volumes are much smaller than expected from the moisture content of ≈ 0.25 weight percent in Asse salt (Figure 2.7). Apparently, most of the brine present as absorbed water (≈ 0.02 weight percent) at grain boundaries, surfaces, etc. migrates to the borehole. It is not established why, in contrast to the generally expected behavior, the brine present in bulk forms such as inclusions does not predominantly contribute to the total volume collected in the borehole. It is possible that at longer times contribution from inclusion migration would become dominant, and then, although the rate of brine migration may be slow, the total volume of brine accumulated may become much larger. Thus, a detailed study of Asse experiment data is required before its results can be used in modeling the performance of repositories in the United States. Also, note that the total moisture content in some of the U.S. salts is much higher than in Asse salt.

In general, grain boundaries in salt provide a path of rapid brine migration. Therefore, brine migration rates are expected to be faster in a fine grained salt deposit than in large single crystals. However, the brine migration rate at a grain boundary or an interface is lower when compressive stresses are present (ORNL-5874, 1982). Biggers and Dayton (ONWI-415, 1982) have studied brine migration in fine grain NaCl samples prepared in laboratory

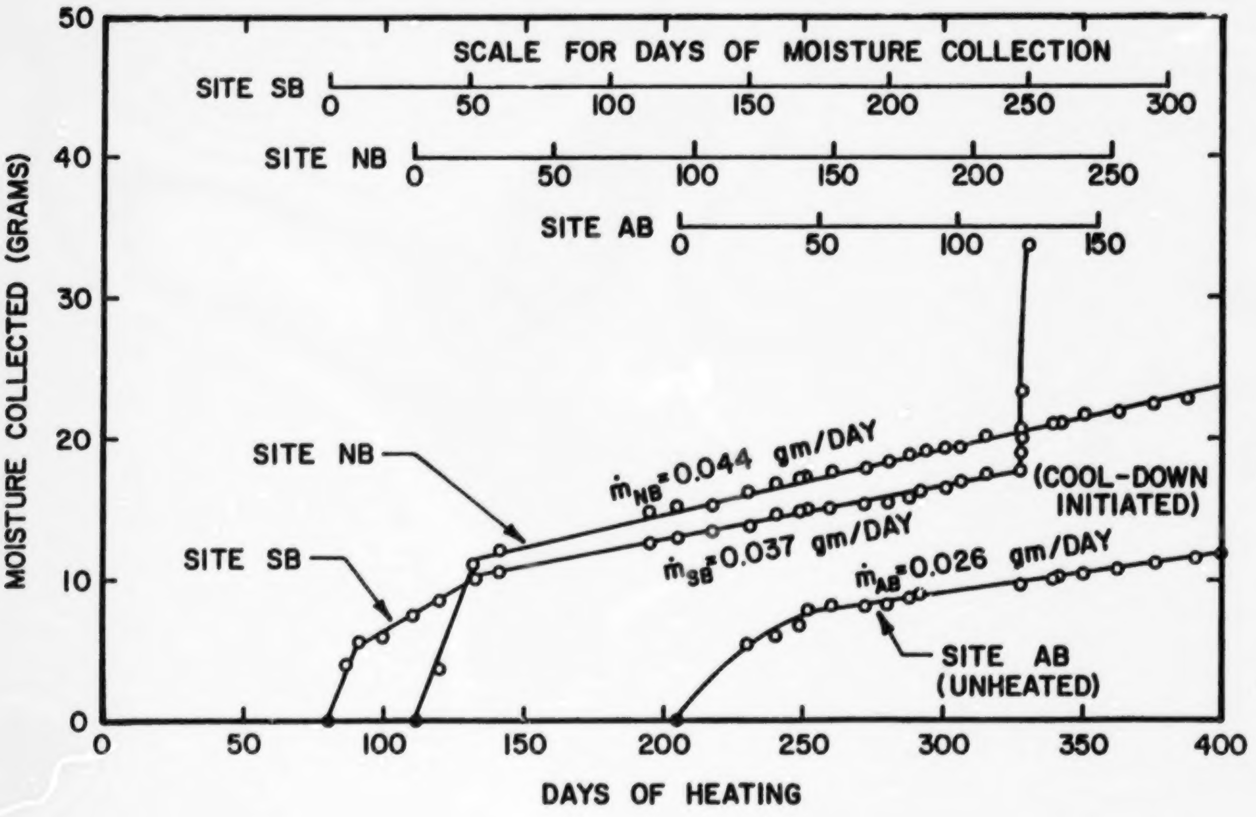


Figure 2.5 Comparison of cumulative moisture collected during the initial 400 days of heating. (ONWI-190(4), 1983)

by hot pressing. The median crystallite size ranged from 0.23 mm to 9.65 mm, and the majority of the samples were pressed to near theoretical density. The schematic design of their test cell in which several thermocouples monitored thermal gradient across the specimen is shown in Figure 2.8. A typical thermal gradient was 3.9 - 7.7°C/cm. Although the salt samples used in this study may be different in composition or under a different thermal gradient than expected in a repository, an important conclusion is that "most conservative estimates indicate (brine migration) rates roughly an order of magnitude greater than those found in single crystal experiments, while other test results indicate up to 2 or 3 orders of magnitude enhancement." Therefore, to obtain a conservative estimate of brine migration rate in a repository, samples with the smallest grain size expected in repository salt should be used in laboratory tests.

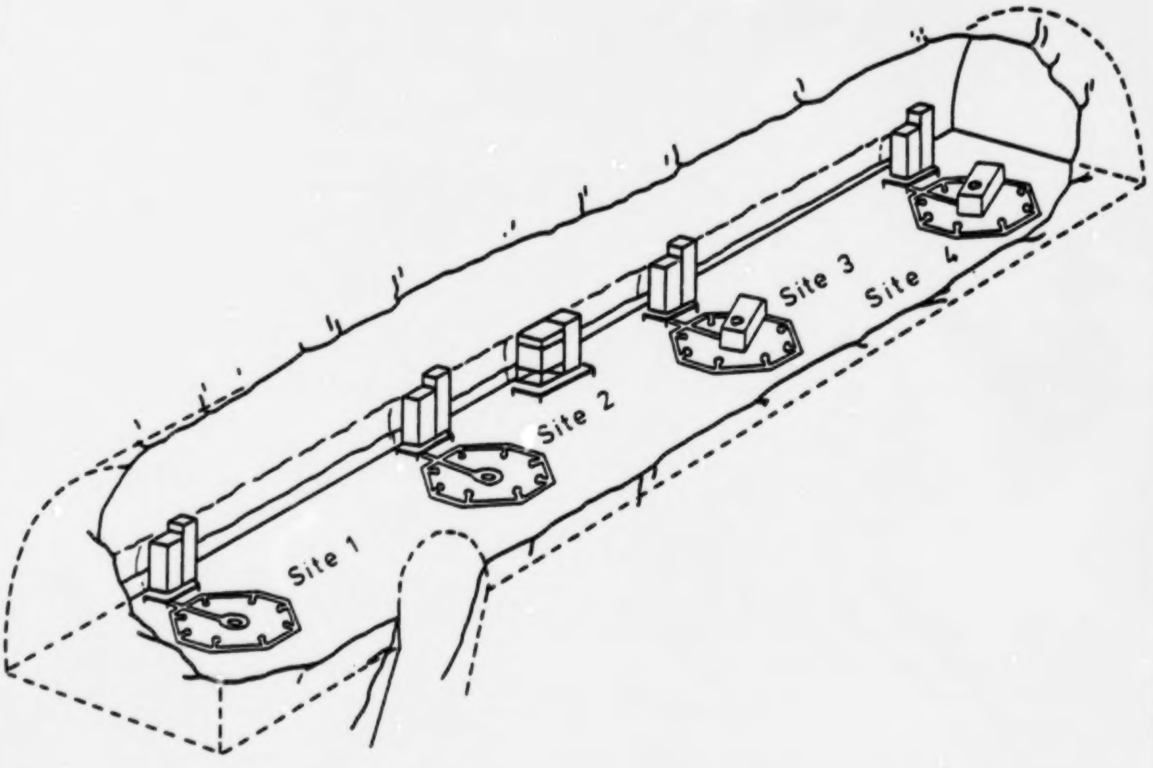


Figure 2.6 Test gallery in Asse Mine (BMI/ONMI-539, 1984)

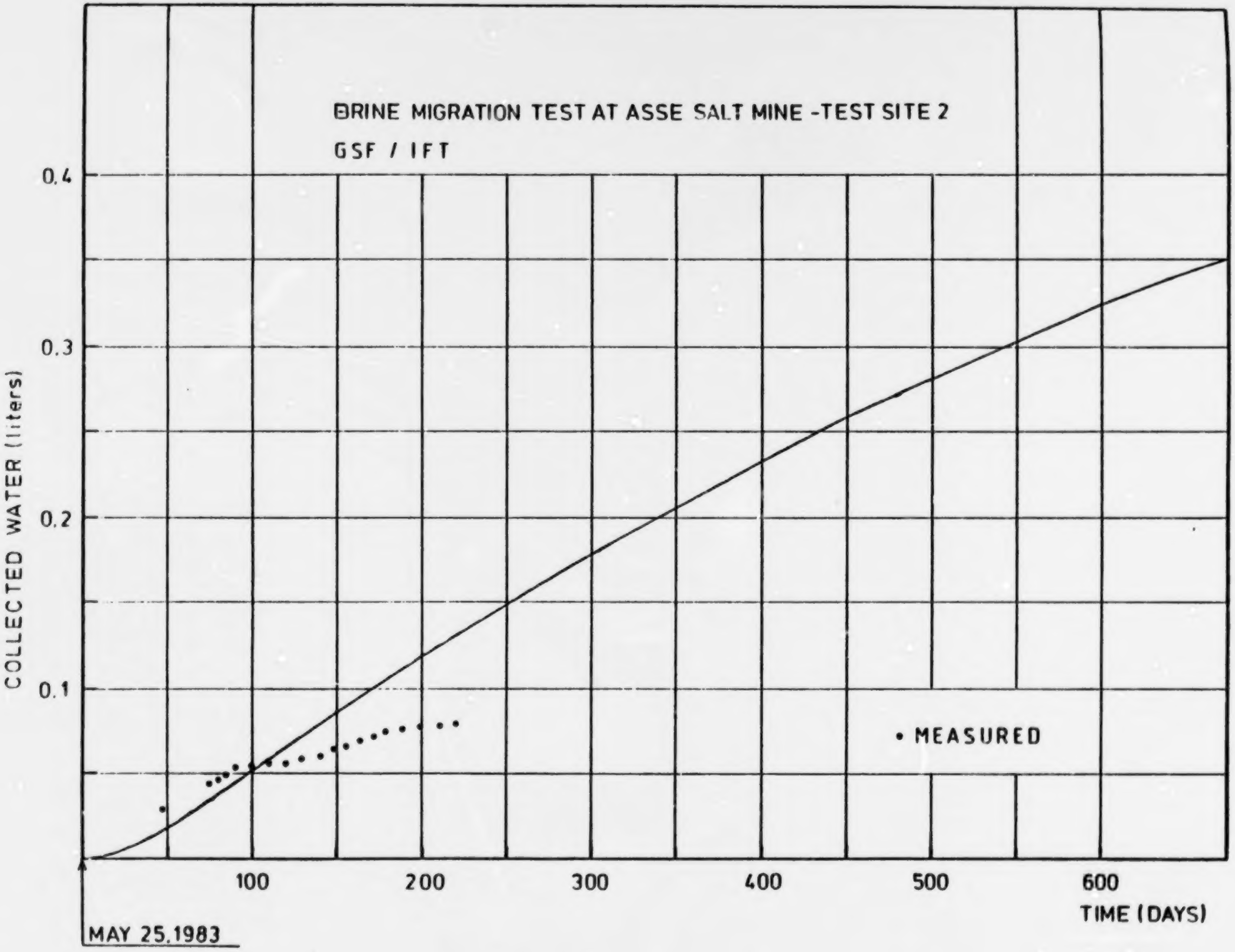
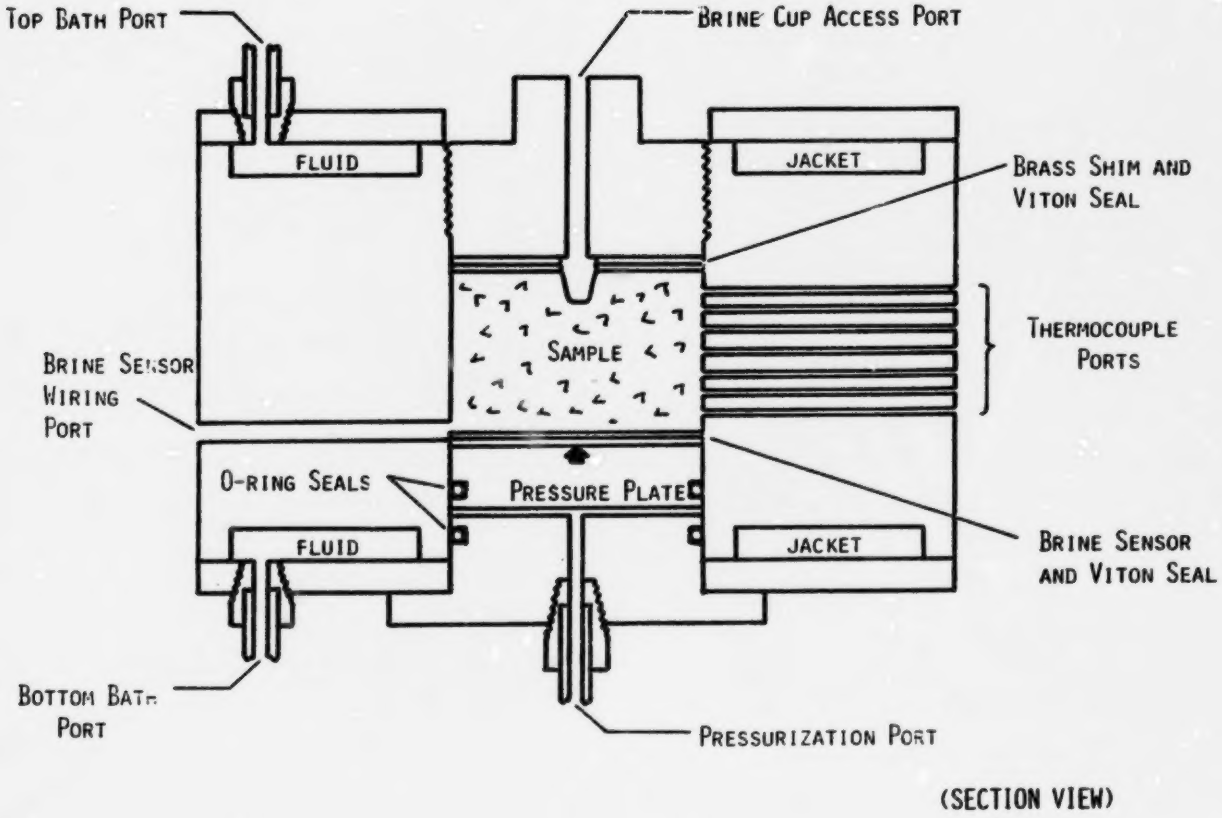


Figure 2.7 Liquid brine inclusion model water production calculated based on assumed 0.06 wt% liquid water in salt. (BMI/ONWI-539, 1984)



TOP BATH PORT
BRINE CUP ACCESS PORT
FLUID
JACKET
BRASS SHIM AND VITON SEAL
THERMOCOUPLE PORTS
SAMPLE
BRINE SENSOR WIRING PORT
O-RING SEALS
PRESSURE PLATE
FLUID
JACKET
BRINE SENSOR AND VITON SEAL
BOTTOM BATH PORT
PRESSURIZATION PORT
(SECTION VIEW)

Figure 2.8 Schematic design of apparatus used in determining brine migration rates in a polycrystalline NaCℓ specimen. (ONWI-415, 1982)

2.2.3.2 Analytical Studies of Brine Migration

Anthony and Cline (1971) considered that the velocity (V) of brine migration in salt consists of four components:

$$V = V_T + V_\sigma - V_K - V_\gamma$$

where V_T = velocity due to the diffusion of brine in a concentration gradient; V_σ is velocity due to the diffusion of brine in a temperature gradient (Soret effect); V_K is velocity due to kinetics of dissolution and crystallization of salt at the salt/brine interface, and V_γ is the velocity due to surface tension at grain boundaries. Chou (1982) compared this model for single crystal salt to the experimental results discussed above. He found that calculated migration rates are much higher than the results of Roedder and Belkin (1980), and those of Bradshaw and Sanchez (1969) have too high a scatter. The discrepancies are attributed to the ommission of an interface kinetics factor (V_K) for which reliable information is not available. His model also does not include the inclusion size dependency on migration rates.

Recently, brine accumulation at a waste package has been estimated using the BRINEMIG or WAPPA computer codes (ONWI-208, 1980, and ONWI-452, 1983), as described in Section 4. Although calculations using these codes are beyond the scope of this work, we note that in these codes the temperature profile in, and moisture content of, the salt (as in inclusions, grain boundaries or water of hydration in clays) are the most important parameters. The results are calculated with and without the assumption of a threshold thermal gradient below which brine would not migrate (Figure 2.9). Such an assumption does not make a major difference in the total brine accumulation, most of which occurs in the first one-hundred years. Brine accumulation for a commercial HLW package containing vitrified waste is somewhat larger than that for spent fuel due to the difference in temperature profiles. The results indicate that brine accumulation in bedded salt can be several times higher than in domal salt because of the much higher moisture content of the former. In this regard we note than an average value of moisture content has been assumed for each type of salt deposit. However, bedded salt can include regions containing high moisture bearing clays. Brine accumulation near such areas may exceed the calculated values unless such regions are carefully avoided, which would require very detailed characterization of each site.

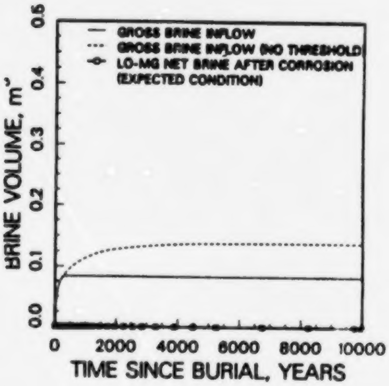


Figure 2.9 Accumulated brine at SFPWR waste package in Richton Dome. (Jansen, G., Jr., 1984)

Whereas some controversy exists concerning the assumption of a threshold temperature gradient below which brine inclusions could not migrate, a more questionable assumption is regarding the distribution of brine around the waste container. For example, in a Palo Duro Basin salt deposit only 2 cm of a 1025 wrought steel container was calculated to be corroded by the brine accummulating uniformly around the container because corrosion would be limited by the lack of availability of brine (Jansen, G., 1984). However, if the available brine reacts with 40% of the overpack surface, the overpack will be breached after 250 years. At present, there is no reason to believe that the available brine will be distributed uniformly or in any other particular fashion around the overpack. Therefore, until a complete failure scenario is established, use of an unlimited brine volume in calculating container corrosion is recommended.

Further uncertainty regarding the corrosion life of the HLW containers exists due to the possibility of localized corrosion. Pitting, hydrogen embrittlement, crevice corrosion or stress corrosion cracking would drastically reduce the above predicted life of an overpack which is based only on uniform corrosion data. These forms of corrosion occur in a localized area of a container but propagate at a much faster rate than uniform corrosion. The amount of data on various forms of localized corrosion in a range of anticipated repository conditions is very limited, and no reliable predictions can be currently made.

2.3 Thermal Environment

The performance of the waste package will be a strong function of temperature. For example, metal corrosion rates and waste form leaching rates usually increase rapidly with temperature. Brine migration rates, also, depend on the temperature gradient as well as the temperature of the host rock. Radiolysis of brine and sorption properties of packing material have complex temperature dependences. Thus, the temperature profile in the vicinity of the waste package, and its variation with time, must be known with sufficient accuracy to establish the conditions needed in testing programs.

The near field thermal environment is determined by the thermal properties of host rock, thermal power of the waste package, the design of the repository, and placement scheme of the waste packages. If such information is available, the temperature profile within a repository, in principle, can be determined by appropriate computer codes. From an additional knowledge of the decay of the radionuclides in the waste, the temperature variation as a function of time can also be calculated. In contrast, in situ determination of the thermal environment is difficult and costly.

Some such experiments have been conducted, or are in progress, at a salt mine at Lyons, Kansas, under Project Salt Vault (ORNL-4555, 1971), at Avery Island (ONWI-190(5), 1983), at Asse mine in Federal Republic of Germany (Prij, J., 1984), and at the Waste Isolation Pilot Plant site in southeastern New Mexico (Molecke, M. A., 1984). These experiments provide information on the thermal and thermo-mechanical properties of host rock, which can be compared with the predictions made from computer calculations. Figure 2.10 shows one

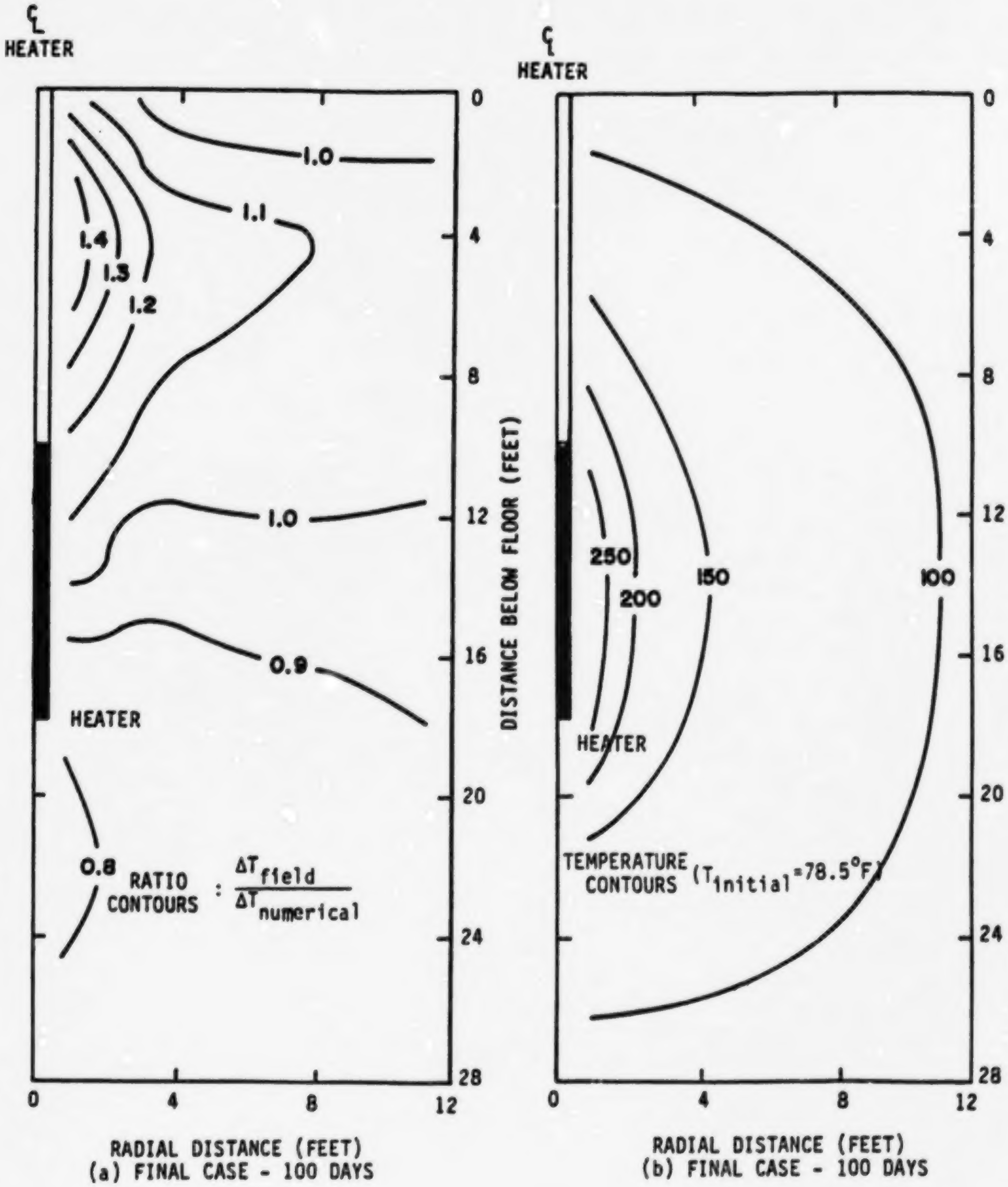


Figure 2.10 Comparison of field-measured and numerically calculated temperatures at 100 days (ONWI-300, 1985)

such comparison between the field-measured data at the Site A of the Avery Island experiment and the numerical results obtained from SPECTROM-41 code (ONWI-300, 1985). The agreement between the field data and numerical results is generally good, but for the volume above the heater the computer code greatly underpredicts the temperatures. The author suggests that the discrepancy is due to the error in field measurements and the assumptions made in the numerical calculations. Nevertheless, the in situ experiments have boundary conditions different from those expected in a repository and, therefore, there is an uncertainty in the recent information available on the thermal environment as calculated using TEMP or TEMPV5 codes (Jansen, G., 1984, and McNulty, E. G., 1985). In this regard the recommendations made by Wagner (ONWI-300-1985) are noteworthy:

> "The single waste canister concept, while suitable for a preliminary experiment, is not entirely representative of the thermo-mechanical response in an actual repository...... The desired experiment should include a multiple heater arrangement. Because of the more complex heater arrangement and the larger area involved, steady-state temperature would not be approached as soon as in the Site A heater test. A more representative thermal response would further increase the confidence in numerical modeling upon the successful agreement between the field-measured and numerically calculated results."

An evaluation of various thermal codes will not be performed here. Nevertheless, a review of available calculations shows that there are large differences among the temperature predictions from different codes. For example, the Westinghouse code calculations (ONWI-438, 1983) using TEMPV5 code underpredict the maximum temperature by 70°C or more, as described for the benchmark comparison in Figure 2.11 and Table 2.6. A recent simplified calculation at Brookhaven National Laboratory to review the thermal analysis for the Swisher repository site suggests that even the TEMPV5 calculations may be underestimating the repository temperatures (Sastre, C., 1984). Sastre observes that the sources of uncertainty in the calculations are thermal conductivity of salt and heat decay curves for the waste form. He concludes that "the method used in TEMPV5 is in principle capable of fair accuracy, even if the changes in thermal diffusivity with temperature are not accommodated in it....The results should be believed only after extensive testing of the numerics." However, because thermal conductivity (diffusivity) of salt can decrease by a factor of 2 to 3 between room temperature and ≈450°C (see Figure 2.12), it is suggested that the temperature dependence of thermal conductivity should be explicitly accomodated or its lowest value be used in determining the maximum temperatures in a repository.

Wagner (ONWI-216, 1982) has shown in the thermal simulation of an Avery Island Heater Test that thermal conductivity is one of the most important parameters which determines the temperature of salt near the heat source. The importance of thermal conductivity of the medium around a waste package has also been demonstrated by Claiborne and others (ORNL/TM-7201, 1980) who calculated temperature profiles corresponding to different properties in the packing materials. Their calculations in Figure 2.13 show that the maximum canister surface temperature of a CHLW package would increase by as much as

300°C when the thermal conductivity of backfill is reduced by a factor of 2. The simple calculations by Sastre (1984) show that a decrease in thermal conductivity of the host rock from 5 W/m-K (used by McNulty, 1985) to 3.5 W/m-K (experimentally observed, (BMI/ONWI-522, 1983)) could cause an increase in canister/overpack temperature of up to 100°C depending on the time after repository closure. From these simplified or indirect calculations, it is clear that thermal conductivity of the host rock salt is a very important parameter. Therefore, a brief review of relevant conductivity information is given below.

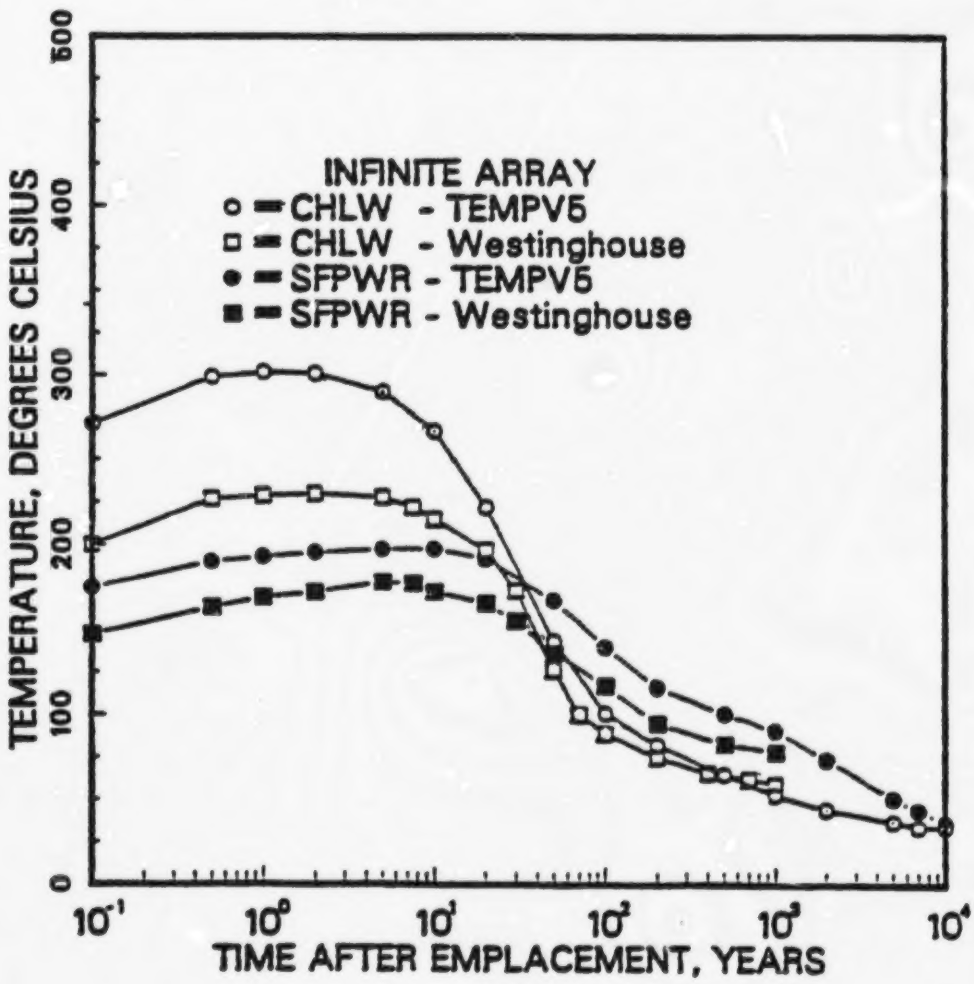


Figure 2.11 Benchmark comparison of TEMPV5 with Westinghouse results at salt-overpack interface. (McNulty, E.G., 1985)

Table 2.6 Benchmark comparison of TEMPV5 and Westinghouse temperatures at salt-overpack interface. (McNulty, E.G., 1985)

Time (years)	Temperature, C			
	CHLW		SFPWR	
	Westinghouse	TEMPV5	Westinghouse	TEMPV5
0.1	200	271.1	147	174.8
0.5	227	298.8	163	190.0
1	229	301.7	169	193.1
2	230	300.8	172	195.4
5	228	290.3	178	197.5
7.5	222		177	
10	215	267.0	172	197.5
20	197	222.2	165	191.8
30	173	187.4	155	183.3
50	126	143.0	136	167.0
70	100	118.9		153.9
100	89	100.8	117	139.6
200	75	82.3	95	116.2
400	66	69.3		103.5
500		64.9	83	100.9
700	62	58.5		96.6
1000	59	52.5	78	90.6
2000		44.4		73.9
5000		37.0		50.7
7000		34.1		43.8
10000		34.0		36.4

Thermal conductivity of rock salt can vary over a large range depending on the origin of salt (see Figure 2.14). Some of the discrepancy among results of different authors, for example shown in Figure 2.14, may be due to the differences in experimental procedures. The thermal conductivity data for rock salt specimens taken from Vacherie Dome, Cypress Creek Dome, Richton Dome, Gibson Dome, and Palo Duro Basin, as obtained by Lagedrost and Capps (BMI/ONWI-522, 1983) are perhaps most relevant to repository conditions. The steady state thermal conductivity of 59 materials in this study was measured

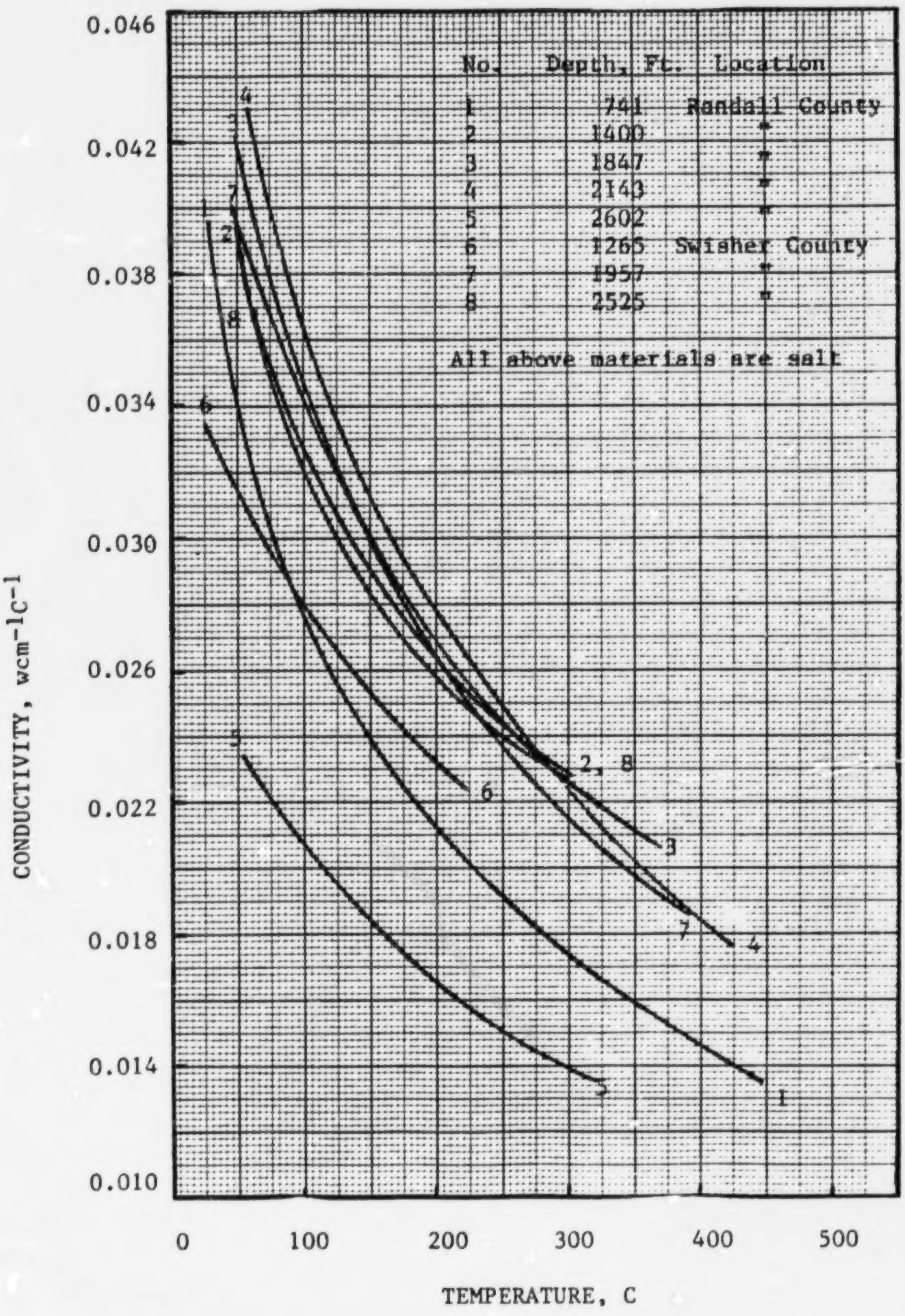


Figure 2.12 Axial thermal conductivity of specimens from Palo Duro Salt Dome, Texas. (BMI/ONWI-522, 1983)

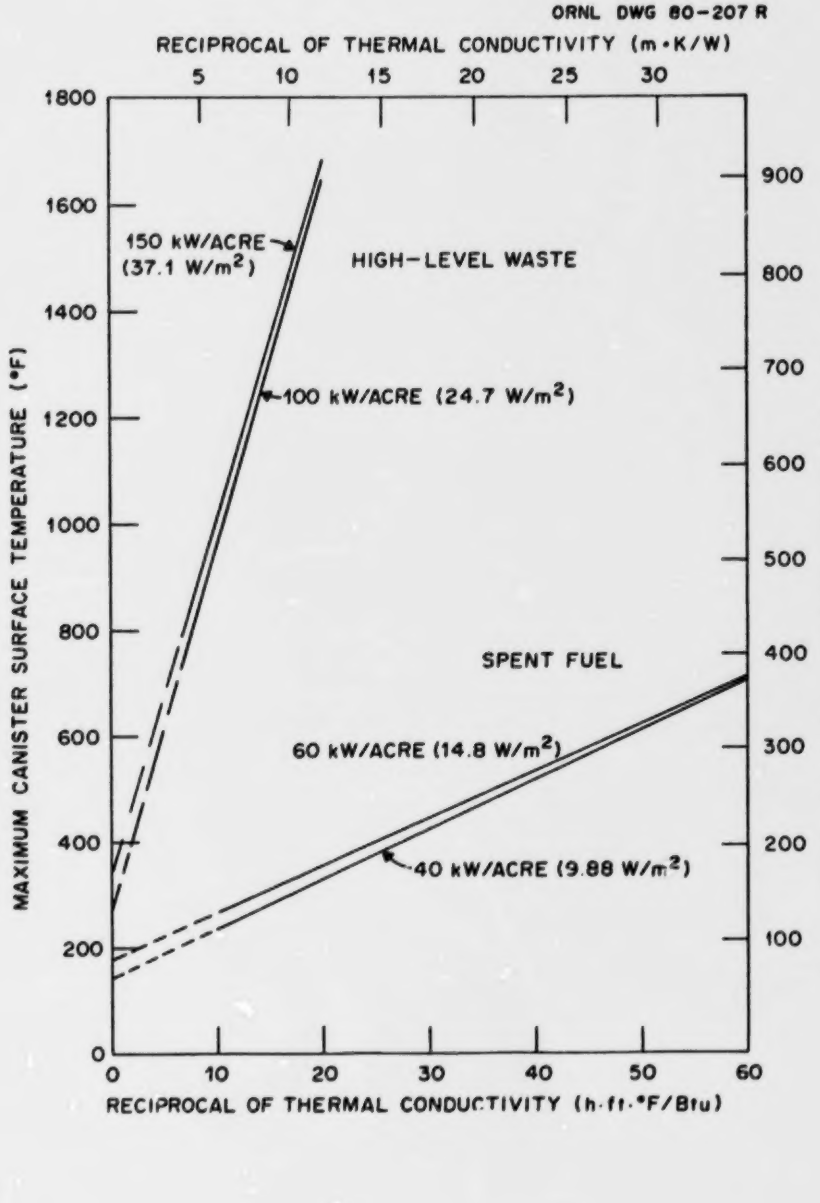


Figure 2.13 Maximum canister surface temperature vs the inverse thermal conductivity for backfill with no air gap. (ORNL/TM-7201, 1980)

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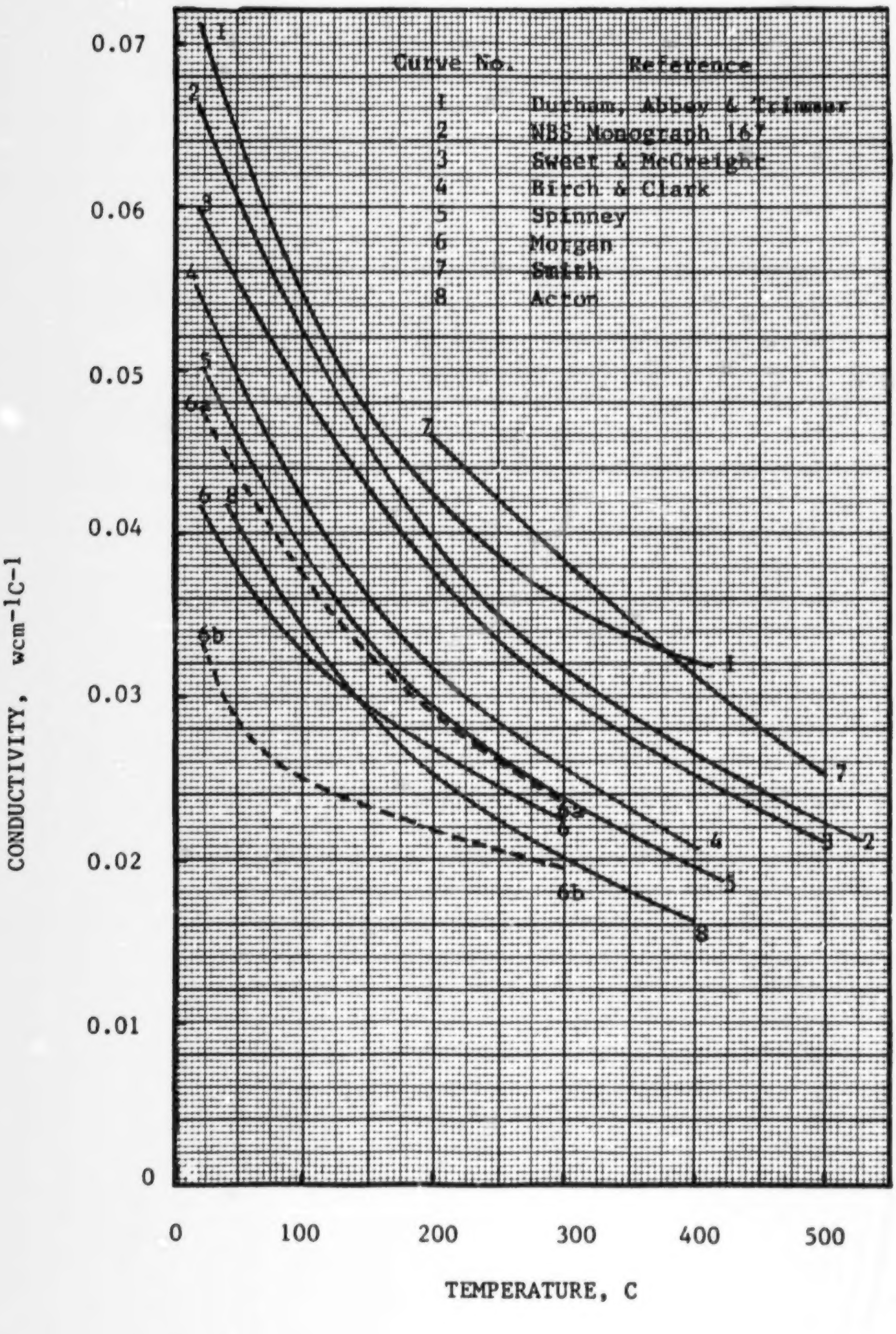

Figure 2.14 Thermal conductivity of crystalline rock salt. (BMI/ONWI-522, 1983)

in the laboratory following the ASTM C-518 (1981) test procedure using a Pyroceram 9606 standard as the heat flow meter. At 50°C the thermal conductivity of different salt specimens varied from 0.022 to 0.046 W/cm-C. At 500°C the range was from 0.012 to 0.027 W/cm-C. There did not appear to be any site specific trend. During sample preparation the authors found that some specimens were extremely friable and a suitable sample could not be obtained. At present the effect of cracking of a friable specimen on the thermal conductivity is not known.

The thermal conductivity values assumed by Claiborne and others (ORNL/TM-7201, 1980) in thermal modeling (see Table 2.7) are considerably higher than the low values measured by Lagedrost and Capps (BMI/ONWI-522, 1983). In the recent thermal modeling with TEMPV5 code, McNulty (1985) used thermal conductivity values which are higher by 40% than the above quoted experimental values. Two rationales are given by McNulty for using higher values of thermal conductivity. First, a correction is made because the tests were conducted using a Pyroceram 9606 calibration standard. However, the quantitative basis for such corrections is neither described by McNulty nor given in the ASTM procedure. Secondly, a 40% increase in conductivity is assumed because it brings the laboratory data into the range of values for other salt specimens. This is not a good scientific justification. McNulty suggested that the laboratory values may be lower than the field values

Table 2.7 Assumed thermal conductivites for salt (ORNL/TM-7201, 1980)

Temperature		Thermal conductivity	
°F	°C	Btu/hr•ft•°F	W/m•K
32	0	3.53	6.11
122	50	2.90	5.02
212	100	2.43	4.20
302	150	2.08	3.60
392	200	1.80	3.11
482	250	1.60	2.77
572	300	1.44	2.49
662	350	1.33	2.30

because of higher in situ stresses at depth. There is some support for this suggestion from the results of salt block experiments (SAND 79-7050, 1980; SAND 79-2226, 1980) but, there are not enough definite reasons to assume a higher value of thermal conductivity than the lowest values observed by Legadrost and Capps (BMI/ONWI-522, 1983). Experiments to verify such assumptions are desirable and it is suggested that the thermal conductivity measurements be made under in situ conditions. If this is not possible, the lowest values observed in the laboratory should be used in determining the temperature profiles in the repository. An experimental verification of the predictions of a code will be needed in developing confidence in the results.

In conclusion, we note that the knowledge of the repository thermal environment is based on assumptions (particularly related to the thermal conductivity values) which might yield low estimates of temperature. The currently used temperature of 150°C by several workers (Westerman, R.E., 1984; Jain, H., 1985a; PNL-SA-12344, 1984) in various waste package component testing may not be the highest temperature under certain repository situations. Similarly, testing at 250°C may not represent accelerating conditions as presumed (Molecke, M. A., 1983). The computer codes developed to predict the thermal environment should consider the use of the lowest available values of thermal conductivity of the host rock and packing material, and explicitly include their temperature and stress dependence.

2.4 Radiation in Salt Repository Environment

Radiation from the waste form (mainly gamma rays during the containment period) is likely to affect waste package performance because of the changes it causes in near-field conditions. The changes would depend on the dose rate and total dose of radiation which, in turn, are dependent on waste package design. For example, in the case of the Westinghouse Reference design, in which a thin-walled container of TiCode-12 is to be used as an overpack, the radiation level at the salt/overpack boundary will be much higher than in the Alternative II (self-shielding) design that uses a thick steel overpack (ONWI-438, 1983). The radiation level at the salt/overpack boundary in these two designs is summarized in Table 2.8 for commercial high level (vitrified) and spent fuel waste packages. At present, the Alternate II design has been adopted by the Salt Repository Project as its reference design (BMI/ONWI-Draft Revision 0, 1984). If this becomes the final design, the effects of radiation on the repository environment will be partly eliminated due to the more than an order of magnitude attenuation of gamma radiation in the steel overpack. As shown in Figure 2.15, the intensity of radiation will further decrease with time and, therefore, the effect on repository conditions could be small. However, in view of the continuing uncertainty with respect to waste package designs, and as a conservative approach for the purpose of this report, the relatively higher radiation dose calculated for the Westinghouse Reference design is assumed, and its consequences with respect to repository conditions are reviewed below.

Both gamma and particle radiation (α, neutrons) cause damage in rock salt and radiolysis of brine. Due to the high penetration, gamma radiation is likely to have the dominant effect on near-field conditions for the first few

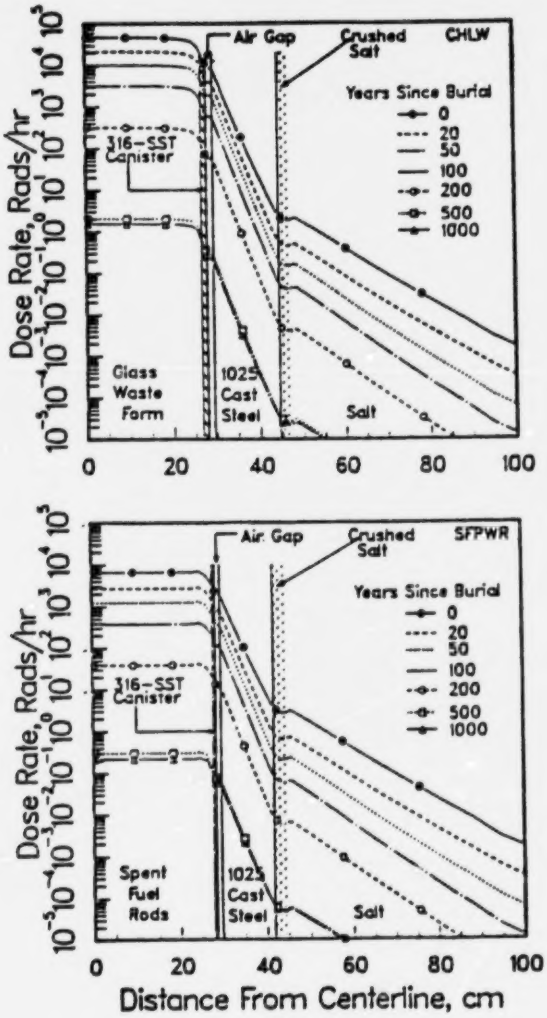

Figure 2.15 Radiation fields due to CHLW and SFPWR at waste package material interface in Alternate II design (DOE/RW-0016, 1984)

hundred years, but in the subsequent tens of thousands of years particle radiation will continue to have significant effects. Since the radiation interacts differently with brine and salt, the effects on each of these are considered separately in the following sections.

Table 2.8 Radiation levels at the surface of the overpack as used in Westinghouse reference and alternate II designs.

	Reference (rem/h)	Alternate II (rem/h)
CHLW:		
neutron	6.8	4.96
gamma	5.3×10^3	95
Spent Fuel:		
neutron	2.85	2.23
gamma	1.09×10^3	85.1

2.4.1 Effect of Radiation on Brine

The effect of radiation on simple salt solutions has been investigated in numerous studies as reviewed by Jenks and others (ORNL-TM-3717, 1972; ORNL-5726, 1981; ORNL-5607, 1980). The reaction of gamma radiation with brine is very complex but the major reaction is the decomposition of water into hydrogen and oxygen accompanied by the production of hydrated electrons, H, OH, H_2O_2, H_3O^+ and OH^-. The generation of several oxidizing and reducing ions and radicals can change the corrosion rates or mechanisms occurring at the brine/overpack interface. Some of the radiolytically produced species are very reactive but too short-lived to be studied by ordinary analytical techniques. Therefore, the information on radiolysis products is largely restricted to the relatively stable species such as H_2, O_2, H_2O_2, Cl_2^-. G values (number of molecules produced per 100 eV of absorbed radiation energy) for these species depend on the temperature and pH of the solution, dose rate, total dose and ambient conditions. For example, $G(H_2)$ for Brine A after a gamma dose of 1 Grad at room temperature is 0.31 when the starting solution pH is 0.3, and 0.41 when the the starting pH is 3.2 (Jain, H., 1985b). Jenks and Walton (ORNL-5726, 1981) observed $G(H_2)$ values for simple brines to vary from 0.44 to 0.49, depending on temperature.

The change in near-field conditions due to brine radiolysis, and its effect on waste package performance is a difficult problem. For example, McCright and Weiss (UCRL-90875, 1984) found a large increase in the corrosion rates of carbon and alloy steels which were tested in J-13 groundwater at 105°C in the presence of a gamma dose rate of 3×10^5 rad/h. Radiolysis of a leachant also gave a several times increase in leach rate of PNL 76-68 glass (McVay, G. L., 1980; 1981) as shown in Table 2.9. In this case the glass was tested in water at 50 and 90°C with a variable pH (adjusted by adding H_2O_2 or HNO_3) and a gamma dose rate of 2.4 Mrad/h. A part of the increase in leach

Table 2.9 Changes in pH and factors of increase in leach rate for individual elements, for 76-68 glass irradiated during leaching at a dose rate of 2.4 Mrad/h (Data of McVay, G.L., 1981, taken from Burns, W.G., 1982).

	Temperature	90°C	50°C	50°C
	Air present or not	Yes	Yes	No
	Element			
	Na	7.0	6.1	5.7
	Cs	4.1	4.0	1.8
	Ca	7.8	7.3	3.7
	Ba	8.0	9.5	3.5
	Sr	7.0	7.0	3.5
	Si	8.4	4.1	3.4
	B .	7.0	4.2	3.3
	Mo	2.8	1.0	3.8
	Zn	420	33	13
	Nd	-	-	>6.5
	Ce	-	-	≈1.0
	Fe	>40.0	>134.0	>3.0
Irradiated specimens	pH before/after	5.7/4.6	5.7/3.3	5.7/6.5
Unirradiated specimens	pH before/after	5.7/8.5	5.7/7.2	5.7/7.2

Specimen sizes approximately 5 mm x 8mm x 2mm
Volume of leachate/glass surface area - 10cm
i.e. Volume of leachate approximately-14 cm^3

rate was attributed to the formation of nitric acid from the radiolysis of air/leachant mixtures, but an increase in the absence of air was explained as being due to the radiolytic production of species such as OH^- and O_2^- radicals (Burns, W. G., 1982). However, in a more recent study under slightly different conditions, an increase at room temperature but a decrease at 90°C in the leach rate due to gamma irradiation has been reported (Yokoyama, H., 1984). In this case the change in leach rate was related to radiation-induced changes in the solution pH, rather than any specific radicals. In general, pH and composition of brine can have a large range depending on irradiation conditions but, at present, only limited information is available on the effect of brine radiolysis on waste form leaching or container corrosion, and there is a special need to understand the mechanisms involved where radiation causes detrimental effects.

From the foregoing discussion it is evident that the stable (non-transient) effects on repository conditions due to radiolysis of brine occur via changes in the pH and Eh of the liquid phase and the generation of gases (primarily hydrogen). In general, the pH of brine approaches a value close to neutral as a result of gamma radiolysis. Jain and others (1985b) found that the pH of initially acidic Brine A (0.3 to 3.2) changed after a gamma dose of 1 Grad at room temperature to 5.3 - 5.9, and suggested that this change could have beneficial effects on metallic corrosion. Gray and Simonson (1985) observed the pH of Permian Basin brine to increase from 2.0 to 3.2, but to decrease from 10.0 to 7.3 as a result of gamma radiolysis at 92°C under much higher doses (15 to 30 Grad). They also found a small effect of plenum gas on the final pH. Thus, the results of experiments conducted so far under very limited conditions suggest a beneficial effect of gamma radiation on the pH of brine, but the extent of pH change may depend on several parameters such as composition, temperature, dose, type of radiation, plenum gas, the presence of containers, rock salt, etc., which needs to be characterized further.

As mentioned above, irradiation of brine solutions produces large amounts of gas together with other stable species. The principal reaction which produces gases during radiolysis is the decomposition of the water molecule into hydrogen and oxygen. The presence of various cations and anions in a brine may affect the final yield of gases by scavenging some of the intermediate species. For example, generation of gases is substantially increased by the presence of Cl^- and Br^- ions which scavenge OH^-. Removal of OH^- retards the back reaction which converts hydrogen into water. Gray and Simonson (1985) have shown that during gamma radiolysis of Permian Basin brine, major scavengers of OH^- are Cl^-, Br^- and SO_4^{--}. There is a synergistic effect among these ions such that individually they are less effective than when present together. Figure 2.16 shows this observation in terms of pressure of radiolytically produced gases as a function of total dose. Note that 0.03 g/L of Br^- + 190 g/L of Cl^- is considerably more effective in gas generation than similar additions of Br^- or Cl^- alone. Further addition of 3.26 g/L of SO_4^{--} to NaCl/NaBr solution gives a pressure vs dose behavior similar to that of Permian Basin brine. Interestingly, replacing one-half of the sodium concentration by magnesium in Permian Basin brine had little effect on the final pressure, thus suggesting that cations are not as important as anions in scavenging reactions.

From the pressure vs dose behavior shown in Figure 2.16, it is important to note that the pressure due to radiolysis of Permian Basin brine approaches a plateau at approximately 100 atmospheres. Further irradiation of brine after reaching the plateau causes no further net pressure increase, presumably due to enhanced reverse reactions. The value of pressure at the plateau or the rate of pressure increase is likely to depend on temperature, pH and chemical composition of the brine. The presence of iron in brine is shown to decrease the pressure of the plateau by a factor of 2, but the mechanism is not understood. In the case of alpha radiolysis of brine, the maximum pressure at the plateau has not been determined, but it is expected to be much higher than in gamma radiolysis (Gray, W. J., 1985). The maximum pressure from the radiolysis of other brines is also not known, but is likely to be about the same as for Permian Basin brine.

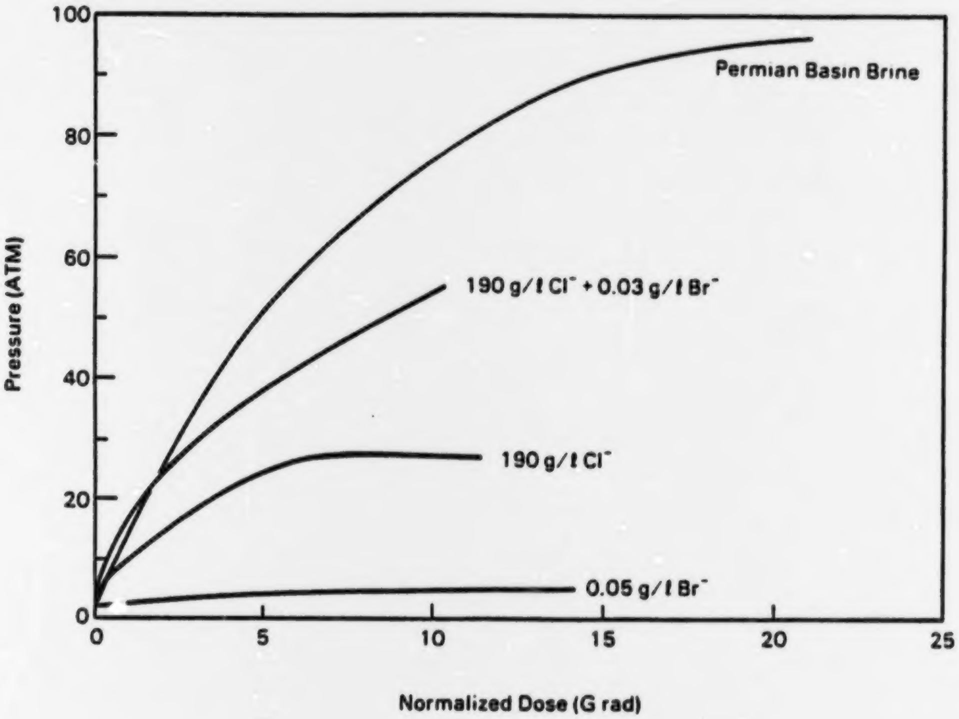

Figure 2.16 Total gas pressure generated by gamma radiolysis at 75°C and 5 Mrad/h of Permian Basin Brine, and NaCl/NaBr solutions in water (Gray, W.J., 1985)

In some gamma radiolysis experiments, the ratio H_2/O_2 in the final gas product has been found to be approximately equal to 2. This has led to the conclusion that equal amounts of oxidizing and reducing species are produced during radiolysis and, therefore, the redox potential of brine should show little change (Pederson, L.R., 1984b; Gray, W.J., 1985). However, the H_2/O_2 ratio has been frequently found to be larger than 2 (ORNL-5726, 1981; Jain, H., 1985b). In such cases the oxidizing species produced in lieu of O_2 have not been identified. Since the solubility of some radionuclides (mostly actinides) or the rate of metallic corrosion strongly depends on the redox potential of the solution, an experimental determination of redox potential and unidentified oxidizing species under the complete range of repository conditions is needed.

For alpha radiolysis of Permian brine, Pederson and others (1984b) reported a H_2/O_2 ratio as high as 10, thus amplifying the need to know the redox conditions even more than in the case of gamma radiolysis. As shown in Figure 2.17, the Eh of their solution increased by 1.0 volt after an alpha dose of 0.9 - 3.6 Mrad, but it is not clear whether this increase is

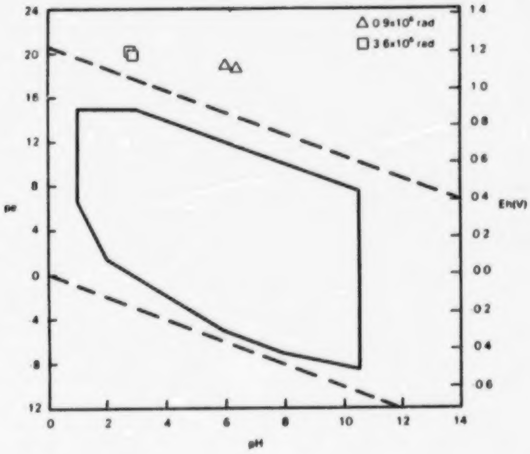

Figure 2.17 Measured and expected pe versus pH in a synthetic saturated Permian Cycle 4 brine. The dark solid lines represent the range of conditions typical of groundwaters. Alpha radiolysis of the saturated brines by ^{244}Cm in a nitrogen atmosphere yielded very oxidizing conditions. (Pederson, L.R., 1984b)

sufficient to explain the high H_2/O_2 ratio. In fact there appears to be little correlation between the change in Eh and H_2/O_2 ratio. Gray and Simonson (1985) also found an increase in Eh of Permian Basin brine after alpha radiolysis at 75°C by 1.2 volts, although the H_2/O_2 ratio was close to the stoichiometric value of 2. These authors suggested that this discrepancy is due to unequal rates of evolution of reducing and oxidizing species which contribute to the H_2/O_2 ratio. To verify this interpretation, Eh vs dose data are required, which would also help in establishing the oxidizing characteristics of brine.

2.4.2 Effect of Radiation on Salt

Levy and co-workers (DOE/TIC-4621, Vol. 1, 1981; Swyler, K.J., 1979; Swyler, K.J., 1980; Lowman, J.M., 1982) and Jenks and co-workers (1975; ORNL-5058, 1977) have extensively studied the effect of gamma radiation on rock salt with special reference to salt repositories. As expected, for a accelerated laboratory testing, a sample is typically irradiated at a dose rate of 10^6 rad/h, or higher. Depending on the temperature of the salt, F-centers or colloidal sodium particles are produced in the crystals. The rate of formation of colloids depends on the dose rate and total dose in a complex manner. Figure 2.18 shows a typical growth behavior of F-centers and sodium colloids in the temperature range of 127 to 228°C.

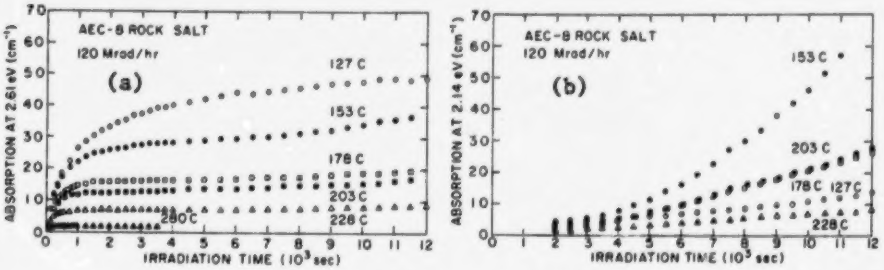

Figure 2.18 Growth of F-centers (a) and sodium colloids (b) (as indicated by optical absorption in rock salt at 2.61 eV and 2.14 eV, respectively) as a function of dose (dose rate = 120 MRad/h) at various temperatures. (Swyler, K.J., 1980)

It is believed that the generation of colloidal sodium is accompanied by the production of Cl_2 or Cl_2^- aggregates in the crystal; the latter species represent an electron trapped at a chlorine molecule. When a salt crystal containing these species comes in contact with water (or brine), OH^-, OCl^-, HOCl, etc. are generated in solution, whereas H_2 and Cl_2 might escape as gases. If Cl_2 gas cannot escape but reacts with water, the increase in pH by the formation of OH^- will be neutralized by hypochlorous and hydrochloric acids, and the final pH will remain close to neutral. However, if Cl_2 escapes and is not able to react with water, the pH of brine can increase to values greater than 10 as shown in Figure 2.19; an irreversible loss of Cl_2 during crushing and annealing makes the resultant solution of pH even higher. Under such highly basic conditions the leaching of a waste form, and possibly the corrosion rates of some container materials, could be enhanced. In fact, the reactions among various radiolytic species such as hydrogen, chlorine, etc. are highly dependent on the experimental conditions and, therefore, testing of waste packages should be conducted over the range of radiation modified repository conditions.

Panno and Soo (1984) examined the effects of gamma irradiation on samples of bedded salt from Carlsbad, New Mexico, as a function of temperature, dose, and whether the salt is dry or wetted with brine. As expected, dissolution of salt irradiated at 125°C resulted in a pH as high as 9.5. The pH value approached saturation at a total dose of approximately 5×10^8 rad. However, when a small amount of brine was present surrounding the salt pieces during irradiation at 125°C, the results were significantly different. In this case sodium colloid formation required a higher dose of radiation. Also, the pH of brine present during irradiation decreased from 7.6 to 3.5, as shown in Figure 2.20. It is interesting to note that, in contrast, in the case of gamma irradiation of brine alone, Jain and others (1985b) noted an increase in pH from an acidic value of 0.3 to a near neutral pH = 5.3. Although the detailed mechanisms of these processes are not known, it is possible that in the case of wet salt gamma irradiation the chlorine produced by radiolysis is dissolved in the surrounding brine which then lowers its pH. The dissolution of thermally released acidic gases from the salt will also cause a decrease in the pH of the brine (see Section 2.2.2). When the salt is dry, chlorine escapes from the salt (Pederson, L. R., 1984b) and the pH of subsequently prepared brine increases due to the reaction of colloidal sodium with water. It should be noted that no chlorine seems to be produced from the radiolysis of brine alone (Jain, H., 1985b).

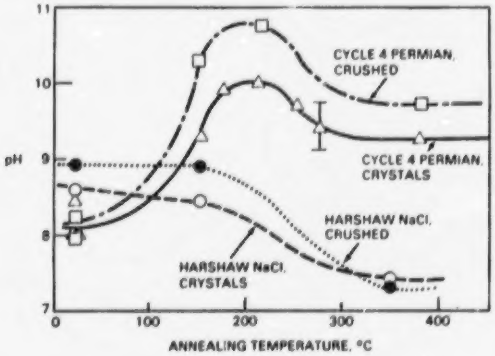

Figure 2.19 Solution pH for 0.1 g salt dissolved in 1.0 mL deionized water that had first been annealed and/or crushed versus annealing temperature. Some irreversible loss of chlorine gas is apparent for the Permian salt, evidenced by elevated pH values. Most of the neutralized sodium and chlorine apparently recombined upon annealing of Harshaw NaCl. The total dose was 5×10^9 rad irradiated at 50°C. (Pederson, L.R., 1984b)

Whereas some information is available on the effect of radiation on rock salt, and its subsequent dissolution in brine as discussed above, it is not known whether the brine migration characteristics of irradiated salt are different from those of unirradiated salt. Brine migration experiments (see Section 2.2.3.1) have been generally carried out under thermal gradient but in the absence of radiation. As an exception, in situ experiments in the Asse mine included a ^{60}Co radiation source, but the data obtained even in the absence of radiation cannot be explained assuming simple migration of moisture

(BMI/ONWI-539, 1984). Thus, there is a strong need to determine the effects of radiation on brine migration in salt under controlled laboratory conditions. The radiation-induced production of gases and colloidal sodium within salt crystals may increase brine migration rates. For example, it is possible that fragmentation of salt due to irradiation, or cracking in irradiated salt on coming in contact with water (Panno, S. V., 1984) would provide additional paths of easy brine inclusion migration.

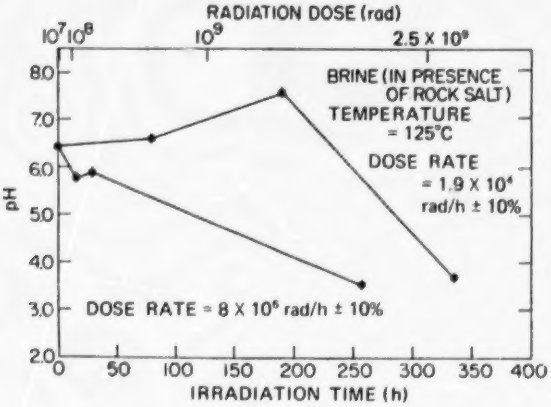

Figure 2.20 The pH of brine irradiated in the presence of rock salt. (Panno, S.V., 1984)

In summary, we note that the presence of radiation can have a range of effects on aqueous conditions in a repository either by radiation damage of salt and its subsequent reaction with brine, or direct radiolysis of brine and adjacent salt. Radiolysis of the brine present as inclusions in salt may not be the same phenomenon as the radiolysis of brine in the laboratory. Dissolution of irradiated salt containing colloidal sodium can increase brine pH to more than 10. If chlorine generated in salt reacts with brine and colloidal sodium is not able to react with it, acidic conditions will prevail. Incidentally, acidic gases can also be generated by simple heating of rock salt (see Section 2.2.2). Gamma radiolysis of brine can generate gas pressures as high as 100 atmospheres, which is predominantly composed of hydrogen. In the case of alpha radiolysis, the pressure is expected to be much higher; its exact value has not been determined. Radiation has a neutralizing effect on high and low values of brine pH, but the present information is very limited. There are indications that radiation, particularly alpha particles, can create highly oxidizing conditions in brine; however, the extent of change in the redox potential of brine as a function of dose, temperature, pH, etc. remains to be determined for most of the range of repository conditions.

2.5 Summary

In a salt repository the containment period for a high level waste package will be primarily determined by the chemical environment, the thermal environment, and the radiation and pressure characteristics, since these factors control the time it takes for a container to fail. Extensive in situ and laboratory testing is required to characterize the chemical environment whereas pressure and radiation characteristics can be calculated from analytical models with reasonable confidence. The thermal environment can also be calculated from analytical models but, at present, input information on the thermal properties of salt needs to be obtained from in situ testing. Testing is also needed to determine the interactive effects among various components of the waste package.

The nature of container corrosion will be affected by the composition and volume of adjacent brine. Various brine compositions which have been used to date in the corrosion and leaching studies can be divided into two categories depending on whether the brine is present as inclusions or is produced from the dissolution of salt in water originating from an external source. The inclusion brine is generally richer in magnesium and, therefore, more corrosive than the dissolution brine; at the Utah site the dissolution brine can also be very high in magnesium. However, laboratory corrosion tests have not always used the highest anticipated magnesium contents for the brine. Also, the test brines have ionic concentrations which are in equilibrium with rock salt at room temperature, but much higher concentrations could be present near the hot surface of the waste canister. If a packing material is to be used around the waste package, its effect on brine composition will need to be determined. Another factor which may affect the brine composition is the presence of gases which are produced when the salt is heated. The effect of these gases (particularly HCl and H_2S) on the integrity of the waste package either directly or via dissolution in brine has not been determined.

It has been suggested by DOE that container corrosion will be limited by the availability of brine, which is then determined by the characteristics of brine migration in salt. At present very limited information is available about the in situ migration of brine, and the correlation between the experimental results and analytical models is questionable. Rapid migration of brine along the grain boundaries in rock salt has not been characterized sufficiently. Larger than predicted accumulation of brine due to this phenomenon, non-uniform distribution of brine around the container, or localized corrosion could reduce the container life considerably.

The thermal environment in a repository, in principle, can be calculated from a knowledge of the thermal properties of salt, radioactive decay characteristics of the waste form and the waste package placement scheme. However, the present computer codes might be underpredicting the repository temperature because appropriate in situ thermal conductivity data are not used. Generally the in situ heater tests to determine the validity of computer codes have been restricted to the single waste canister concept whereas in an actual repository the boundary conditions and thermomechanical response will be far more complicated.

If a self-shielding waste package is not used, radiation, through its interaction with brine and salt, can change repository conditions and influence the corrosion. Although gamma radiation appears to drive brine towards neutral pH, it also produces large amounts of hydrogen which can cause embrittlement in some metals. There is also very little information available on the effect of radiation on the Eh of brine. In addition, most of the information on radiolytic products concern stable species although the corrosion processes can also be affected by highly reactive transient species. Interaction of radiation with salt produces colloidal sodium and chlorine gas or aggregates of Cl_2^-. Dissolution of the irradiated salt in water produces acidic to highly alkaline conditions and this will have an effect on corrosion. At present, the irradiation tests have been carried out under a limited range of the physical conditions, temperature, dose rate and total dose. Much more comprehensive testing will be required before the conditions around a waste package can be specified.

2.6 Recommendations for Future Work

The semi-quantitative estimates of waste package conditions in a salt repository, as an example, are given in Table 1.2 of Section 1. However, some of these estimates are based on indirect calculations, or data which are not representative of in situ conditions. To obtain a conservative estimate of such conditions, the following recommendations are made and the areas of further research are identified on the basis of the review of information on the chemical and thermal environments, and the effect of radiation on the chemical environment:

- A composition of brine needs to be identified which would represent the most corrosive solution expected in a salt repository. In particular, the ionic concentration in solution should be representative of brine in contact with the salt at repository temperature, not at room temperature as assumed currently. Corrosion tests should be carried out in this 'high temperature' brine. Although Mg^{++} concentration has been linked to the corrosivity of a brine, the system has not been characterized sufficiently to ignore the effects of other ions, radiation and different components of the waste package. The concentration of magnesium ions in brine, and their effectiveness as corrosive species as a function of composition needs to be established. To identify the most corrosive composition, various brines suggested by Hubbard and compositions representative of other sites should be reacted with different waste package components under appropriate temperature and radiation conditions and the resulting changes (e.g. in pH and composition) determined. From the knowledge of corrosion susceptibility of a metal to various chemical species, the most corrosive composition can be inferred. Then, this brine may be used in the screening of alloys. Once the alloy composition for waste canisters has been finalized, corrosion tests in a few selected brine composition may be conducted to obtain reliable data.

- Interaction effects between brine and the packing material (if any) should be considered in simulating the repository conditions.

- The range of composition and volume of the gases generated during the heating and irradiation of salt/brine combinations need to be determined to evaluate their effect on corrosion.

- The rate of brine migration needs to be determined under in situ conditions. In the laboratory, the rates should be determined for the appropriate range of temperature gradients, and the inclusion size. Salt samples of varying grain size should be tested, to evaluate the rapid migration of brine along the grain boundaries.

- The greatest uncertainty in determining the thermal environment is due to the lack of appropriate data on the thermal conductivity of salt and its temperature dependence. Therefore, in situ measurements of thermal conductivity should be carried out at the representative sites and its lowest value be used in analytical models.

- Although preliminary experiments show that radiation has a moderating effect on the pH of brine, this needs to be verified for the complete range of repository conditions.

- The effect of radiation on the Eh of brine needs to be determined more precisely and the oxidizing species produced by radiolysis need to be identified.

- The maximum gas pressure generated from the alpha radiolysis of brine needs to be determined.

- At present there is very little information available on the transient species produced during radiolysis. These species are generally very reactive and, therefore, can affect the corrosion processes.

- Finally, since high lithostatic pressures will be present at the waste package, some experiments concerning the repository conditions should be carried out either under in situ pressures or in a high pressure laboratory environment. Thermal conductivity and brine migration rates will perhaps be influenced by such external pressures.

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3. REVIEW OF TESTING PROCEDURES AND DATA ON COLLOID FORMATION AND THE SOLUBILITIES OF RADIONUCLIDES IN ANTICIPATED REPOSITORY WATERS

3.1 Introduction

The objective of this Subtask is to review and evaluate available testing information on the solubility of nuclides which predominate after the containment period is over, and the formation and properties of colloidal systems that are pertinent to anticipated repository conditions.

Several important radionuclides, mainly actinides, will have appreciable inventories during the 10,000-year period required for predicting controlled release rates. For a major portion of this period, releases may occur in an environment containing container corrosion products, chemically and physically altered packing material, hydrated high-surface-area glass (or high-surface-area spent fuel), etc. In such systems, unknown but potentially large quantities of radionuclides may also be absorbed on and transported by suspended or colloidal materials from corrosion products, packing material, or other altered barrier system materials.

Spent fuel from light water reactors contains all of the long-lived and stable nuclides that result from in-reactor operation. Tables 3.1 and 3.2 show an inventory of nuclides at various times from discharge. These tables are adapted from ORIGEN-2 calculated values presented in ORNL/TM-6008 (1977), (BNL-NUREG-51694, Vol. 7, 1984). Based on the calculations for the inventories at 300 years, 1000 years, and 10,000 years, the bulk of the activity (greater than 89%) in spent fuel is attributable to the isotopes of Am, Pu, and Np. A non-actinide that contributes significantly to the activity is Tc. Therefore, in this present study, the following elements were selected for review: Am, Pu, Np, U and Tc. Uranium has been included since it is the matrix material in the spent fuel and also its leaching and solubility studies can yield useful information that is applicable to other radionuclides. Some work in this area is discussed in Section 3.2.4

The stabilities of major radionuclide ions in a solution are:

$$UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+} > AmO_2^{2+};\ Am^{3+} > Pu^{3+} >> Np^{3+},\ U^{4+}.$$

(Cotton and Wilkinson, 1980)

A comparison of various actinide ions is given in Table 3.3 It must be noted also that for comparatively short-lived isotopes decaying by alpha emission or spontaneous fission, heating and chemical effects due to the high level of radioactivity occur in both solids and aqueous solutions. Radiation-induced decomposition of water leads to H and OH radicals, hydrogen peroxide production, etc., and in solution higher oxidation states such as Pu^{5+}, Pu^{6+}, and Am^{4+}, Am^{5+} and Am^{6+} are reduced. However, the steady state condition may not be reached here.

Table 3.1 Activity of radionuclides in a BWR fuel rod irradiated to an average burnup of 27,500 MWd/MTU as a function of age.[a,b]

10 Years From Discharge		300 Years From Discharge		1000 Years From Discharge			10,000 Years From Discharge	
Nuclide	Activity (Ci)	Nuclide	Activity (Ci)	Nuclide	Activity (Ci)	[Weight (g) in Parentheses]	Nuclide	Activity (Ci)
^{241}Pu	2.013E02							
^{137}Cs	1.989E02							
^{137m}Ba	1.881E02							
^{90}Y	1.419E02							
^{90}Sr	1.419E02							
^{147}Pm	2.435E01							
^{85}Kr	1.177E01							
^{134}Cs	1.117E01							
^{154}Eu	1.082E01							
^{238}Pu	4.732E00	^{241}Am	7.210E00	^{241}Am	2.351E00	(7.252E-01)		
^{241}Am	4.443E00	^{240}Pu	1.313E00	^{240}Pu	1.222E00	(5.393E00)		
^{155}Eu	3.683E00							
^{125}Sb	3.405E00							
^{244}Cm	2.051E00							
^{60}Co	1.776E00							
^{240}Pu	1.347E00							
^{106}Ru	1.299E00							
^{106}Rh	1.299E00							
^{3}H	1.182E00							
^{239}Pu	8.619E-01	^{239}Pu	8.551E-01	^{239}Pu	8.389E-01	(1.367E01)	^{239}Pu	6.546E-01
^{151}Sm	8.524E-01	^{238}Pu	4.984E-01				^{240}Pu	4.857E-01
^{125m}Te	8.316E-01	^{137}Cs	2.502E-01					
^{144}Ce	3.422E-01	^{137m}Ba	2.367E-01					
^{144}Pr	3.422E-01	^{90}Y	1.110E-01					
^{63}Ni	3.381E-01	^{90}Sr	1.109E-01					
^{55}Fe	2.375E-01							
^{243}Am	3.568E-02	^{151}Sm	9.803E-02	^{243}Am	3.262E-02	(1.761E-01)	^{99}Tc	3.149E-02
^{239}Np	3.568E-02	^{63}Ni	3.803E-02	^{239}Np	3.262E-02	(1.415E-07)	^{243}Am	1.443E-02
^{99}Tc	3.254E-02	^{243}Am	3.476E-02	^{99}Tc	3.243E-02	(1.902E00)	^{239}Np	1.443E-02
^{243}Cm	1.034E-02	^{239}Np	3.476E-02					
		^{99}Tc	3.251E-02					
^{93}Zr	8.524E-03	^{93}Zr	8.522E-03	^{93}Zr	8.518E-03	(3.321E00)	^{93}Zr	8.462E-03
^{242}Pu	4.298E-03	^{93m}Nb	8.096E-03	^{93m}Nb	8.092E-03	(2.860E-05)	^{93m}Nb	8.040E-03
^{14}C	4.176E-03	^{234}U	4.497E-03	^{234}U	4.670E-03	(7.543E-01)	^{234}U	4.576E-03
^{144m}Pr	4.106E-03	^{242}Pu	4.297E-03	^{242}Pu	4.292E-03	(1.100E00)	^{242}Pu	4.222E-03
^{93m}Nb	3.948E-03	^{14}C	4.032E-03	^{14}C	3.705E-03	(8.307E-04)	^{237}Np	2.978E-03
^{121m}Sn	3.357E-03	^{242}Cm	2.749E-03	^{237}Np	2.511E-03	(3.559E00)	^{233}Pa	2.978E-03
^{234}U	2.968E-03	^{59}Ni	2.387E-03	^{233}Pa	2.511E-03	(1.210E-07)	^{59}Ni	2.195E-03
^{59}Ni	2.394E-03	^{126m}Sb	1.833E-03	^{238}Pu	2.383E-03	(1.370E-04)	^{126m}Sb	1.714E-03
^{126m}Sb	1.838E-03	^{126}Sn	1.833E-03	^{59}Ni	2.373E-03	(3.130E-02)	^{126}Sn	1.714E-03
^{126}Sn	1.838E-03	^{237}Np	1.529E-03	^{126m}Sb	1.825E-03	(2.324E-11)	^{14}C	1.247E-03
^{119m}Sn	1.150E-03	^{233}Pa	1.529E-03	^{126}Sn	1.825E-03	(6.426E-02)	^{135}Cs	1.034E-03
^{135}Cs	1.037E-03	^{135}Cs	1.037E-03	^{135}Cs	1.037E-03	(1.174E00)		
^{79}Se	9.860E-04	^{79}Se	9.830E-04	^{79}Se	9.757E-04	(1.400E-02)	^{234m}Pa	9.225E-04
^{94}Nb	9.364E-04	^{94}Nb	9.251E-04	^{234m}Pa	9.225E-04	(1.355E-12)	^{234}Th	9.225E-04
^{234m}Pa	9.225E-01	^{234m}Pa	9.225E-04	^{234}Th	9.225E-04	(3.983E-08)	^{238}U	9.225E-04
^{234}Th	9.225E-04	^{234}Th	9.225E-04	^{238}U	9.225E-04	(2.768E03)	^{79}Se	8.863E-04
^{238}U	9.225E-04	^{238}U	9.225E-04	^{94}Nb	9.030E-04	(4.745E-03)	^{233}U	8.568E-04
^{237}Np	7.141E-04	^{236}U	6.230E-04	^{236}U	6.487E-04	(1.022E04)	^{94}Nb	6.608E-04
^{233}Pa	7.141E-04	^{107}Pd	2.760E-04	^{151}Sm	5.295E-04	(2.011E-05)	^{230}Th	3.822E-04
^{236}U	6.117E-04	^{126}Sb	2.567E-04	^{107}Pd	2.760E-04	(5.778E-01)	^{210}Bi	2.975E-04
^{107}Pd	2.760E-04	^{241}Pu	2.511E-04	^{126}Sb	2.556E-04	(3.082E-09)	^{214}Bi	2.975E-04
^{126}Sb	2.573E-04			^{63}Ni	1.968E-04	(3.156E-06)	^{210}Pb	2.975E-04
^{153}Gd	1.112E-04			^{243}Cm	1.129E-04	(3.400E-08)	^{214}Pb	2.975E-04
							^{210}Po	2.975E-04
							^{214}Po	2.975E-04
							^{218}Po	2.975E-04
							^{226}Ra	2.975E-04
							^{222}Rn	2.975E-04
							^{107}Pd	2.757E-04
							^{126}Sb	2.400E-04
^{54}Mn	9.205E-05	^{129}I	7.619E-05	^{129}I	7.619E-05	(4.669E-01)	^{129}I	7.616E-05
^{129}I	7.619E-05	^{121m}Sn	6.014E-05	^{230}Th	3.855E-05	(1.972E-03)	^{36}Cl	3.054E-05
^{36}Cl	3.122E-05	^{36}Cl	3.121E-05	^{241}Pu	3.770E-05	(3.351E-07)	^{241}Am	1.903E-05
^{93}Mo	2.270E-05	^{244}Cm	3.083E-05	^{36}Cl	3.116E-05	(9.656E-04)	^{241}Pu	1.773E-05
^{65}Zn	1.044E-05	^{93}Mo	2.124E-05	^{93}Mo	1.806E-05	(4.695E-07)	^{93}Mo	2.257E-06
^{228}Th	3.175E-07	^{230}Th	[illegible].035E-05	^{210}Bi	6.990E-06	(5.633E-11)	[illegible]Pu	4.097E-22
^{123}Sn	5.052E-09	^{214}Bi	6.084E-07	^{214}Bi	6.990E-06	(1.566E-13)	^{243}Cm	1.698E-22
^{113m}In	1.294E-09	^{214}Pb	6.084E-07	^{210}Pb	6.990E-06	(8.369E-08)		
^{113}Sn	1.294E-09	^{214}Po	6.084E-07	^{214}Pb	6.990E-06	(2.132E-13)	TOTAL	1.250E00
^{214}Pb	8.725E-10	^{218}Po	6.084E-07	^{210}Po	6.990E-06	(1.555E-09)		
^{214}Po	8.725E-10	^{226}Ra	6.084E-07	^{214}Po	6.990E-06	(2.175E-20)		
^{218}Po	8.725E-10	^{222}Rn	6.084E-07	^{218}Po	6.990E-06	(7.673E-14)		
^{226}Ra	8.725E-10	^{210}Bi	4.963E-07	^{226}Ra	6.990E-06	(7.073E-06)		
^{222}Rn	8.725E-10	^{210}Pb	4.963E-07	^{222}Rn	6.990E-06	(4.539E-11)		
^{214}Bi	8.725E-10	^{210}Po	4.963E-07	^{137}Cs	2.497E-08	(2.868E-10)		
^{210}Pb	1.130E-10	^{3}H	9.440E-08	^{137m}Ba	2.362E-08	(4.390E-17)		
^{210}Bi	1.130E-10	^{85}Kr	8.598E-08	^{121m}Sn	3.651E-09	(9.383E-11)		
^{210}Po	1.130E-10	^{154}Eu	7.628E-10	^{90}Sr	3.519E-09	(2.652E-11)		
^{95}Nb	1.137E-13	^{60}Co	4.495E-17	^{90}Y	3.519E-09	(6.468E-15)		
^{95}Zr	5.272E-14	^{155}Eu	2.342E-18	^{244}Cm	7.029E-17	(8.636E-19)		
^{160}Tb	1.177E-14			^{3}H	6.960E-25	(7.186E-29)		
^{58}Co	9.560E-16	TOTAL	1.088E01	^{85}Kr	1.973E-27	(5.062E-30)		
^{91}Y	3.586E-16							
^{95m}Nb	4.963E-17			TOTAL	4.362E00			
^{89}Sr	1.130E-18							
^{103m}Rh	5.006E-25							
^{103}Ru	5.002E-25							
TOTAL	9.597E02							

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[a] This table is adapted from ORIGEN-2 calculated values presented in ORNL/TM-6008 (1977) for an 8 x 8 assembly assumed to contain 63 rods.

[b] Nuclides are listed in order of decreasing activity. Activity due to ^{235}U is not included in this table. It is estimated to be ≈4.623E-03 Ci per fuel rod.

Table 3.2 Activity of radionuclides in a PWR fuel rod irradiated to an average burnup of 33,000 MWd/MTU as a function of age.[a,b]

10 Years From Discharge		300 Years From Discharge		1000 Years From Discharge			10,000 Years From Discharge	
Nuclide	Activity (Ci)	Nuclide	Activity (Ci)	Nuclide	Activity (Ci)	[Weight (g) in Parentheses]	Nuclide	Activity (Ci)
^{137}Cs	1.863E02							
^{137m}Ba	1.763E02							
^{241}Pu	1.749E02							
^{90}Y	1.338E02							
^{90}Sr	1.338E02							
^{147}Pm	2.199E01							
^{134}Cs	1.208E01							
^{85}Kr	1.122E01							
^{154}Eu	1.073E01							
^{238}Pu	4.907E00	^{241}Am	6.221E00	^{241}Am	2.029E00	(6.258E-01)		
^{60}Co	4.763E00	^{240}Pu	1.130E00	^{240}Pu	1.051E00	(4.638E00)		
^{241}Am	3.794E00							
^{155}Eu	3.704E00							
^{125}Sb	2.964E00							
^{244}Cm	2.371E00							
^{63}Ni	1.392E00							
^{106}Rh	1.333E00							
^{106}Ru	1.333E00							
^{240}Pu	1.157E00							
^{3}H	1.052E00							
^{55}Fe	8.765E-01	^{239}Pu	6.926E-01	^{239}Pu	6.799E-01	(1.108E01)	^{239}Pu	5.314E-01
^{151}Sm	8.015E-01	^{238}Pu	5.157E-01				^{240}Pu	4.179E-01
^{125m}Te	7.239E-01	^{137}Cs	2.345E-01					
^{239}Pu	6.980E-01	^{137m}Ba	2.218E-01					
^{144}Ce	3.719E-01	^{63}Ni	1.565E-01					
^{144}Pr	3.719E-01	^{90}Sr	1.048E-01					
		^{90}Y	1.048E-01					
^{243}Am	3.738E-02	^{151}Sm	9.221E-02	^{243}Am	3.617E-02	(1.845E-01)	^{99}Tc	2.905E-02
^{239}Np	3.738E-02	^{243}Am	3.641E-02	^{239}Np	3.617E-02	(1.482E-07)	^{243}Am	1.512E-02
^{99}Tc	3.003E-02	^{239}Np	3.641E-02	^{99}Tc	2.993E-02	(1.755E00)	^{239}Np	1.512E-02
^{59}Ni	1.038E-02	^{99}Tc	3.000E-02	^{59}Ni	1.029E-02	(1.357E-01)		
		^{59}Ni	1.035E-02					
^{242}Cm	7.603E-03	^{93}Zr	7.092E-03	^{93}Zr	7.092E-03	(2.766E00)	^{59}Ni	9.520E-03
^{93}Zr	7.097E-03	^{93m}Nb	6.739E-03	^{93m}Nb	6.738E-03	(2.382E-05)	^{93}Zr	7.045E-03
^{144m}Pr	4.463E-03	^{234}U	4.237E-03	^{234}U	4.616E-03	(7.133E-01)	^{93m}Nb	6.691E-03
^{242}Pu	4.066E-03	^{242}Pu	4.064E-03	^{242}Pu	4.059E-03	(1.041E00)	^{234}U	4.324E-03
^{14}C	3.355E-03	^{14}C	3.239E-03	^{14}C	2.976E-03	(6.673E-04)	^{242}Pu	3.994E-03
^{93m}Nb	3.237E-03	^{94}Nb	3.028E-03	^{94}Nb	2.955E-03	(1.553E-02)	^{237}Np	2.664E-03
^{94}Nb	3.059E-03	^{242}Cm	2.021E-03	^{238}Pu	2.386E-03	(1.371E-04)	^{233}Pa	2.664E-03
^{234}U	2.656E-03	^{126m}Sb	1.750E-03	^{237}Np	2.261E-03	(3.205E00)	^{94}Nb	2.163E-03
^{126m}Sb	1.753E-03	^{126}Sn	1.750E-03	^{233}Pa	2.261E-03	(1.089E-07)	^{126m}Sb	1.636E-03
^{126}Sn	1.753E-03	^{237}Np	1.413E-03	^{126}Sn	1.762E-03	(6.134E-02)	^{126}Sn	1.636E-03
		^{233}Pa	1.413E-03	^{126m}Sb	1.741E-03	(2.217E-11)	^{14}C	1.002E-03
^{79}Se	9.255E-04	^{79}Se	9.225E-04	^{79}Se	9.157E-04	(1.314E-02)	^{135}Cs	8.377E-04
^{135}Cs	8.402E-04	^{135}Cs	8.402E-04	^{135}Cs	8.402E-04	(9.510E-01)	^{79}Se	8.319E-04
^{234m}Pa	7.113E-04	^{234m}Pa	7.113E-04	^{63}Ni	8.025E-04	(1.300E-05)	^{236}U	7.796E-04
^{234}Th	7.113E-04	^{234}Th	7.113E-04	^{234m}Pa	7.113E-04	(1.065E-12)	^{234m}Pa	7.113E-04
^{238}U	7.113E-04	^{238}U	7.113E-04	^{234}Th	7.113E-04	(3.071E-08)	^{234}Th	7.113E-04
^{237}Np	7.108E-04	^{236}U	5.784E-04	^{238}U	7.113E-04	(2.134E03)	^{238}U	7.113E-04
^{233}Pa	7.108E-04	^{107}Pd	2.540E-04	^{236}U	6.005E-04	(9.461E00)	^{230}Th	3.612E-04
^{236}U	5.686E-04	^{126}Sb	2.450E-04	^{151}Sm	4.985E-04	(1.893E-05)	^{210}Bi	2.810E-04
^{119m}Sn	4.904E-04	^{241}Pu	2.332E-04	^{107}Pd	2.539E-04	(5.315E-01)	^{214}Bi	2.810E-04
^{107}Pd	2.540E-04			^{126}Sb	2.438E-04	(2.940E-09)	^{210}Pb	2.810E-04
^{126}Sb	2.455E-04						^{214}Pb	2.810E-04
							^{218}Po	2.810E-04
							^{214}Po	2.810E-04
							^{210}Po	2.810E-04
							^{222}Rn	2.810E-04
							^{226}Ra	2.810E-04
							^{107}Pd	2.537E-04
							^{126}Sb	2.291E-04
^{129}I	7.078E-05	^{129}I	7.078E-05	^{242}Cm	8.304E-05	(2.500E-08)	^{129}I	7.074E-05
^{93}Mo	6.828E-05	^{93}Mo	6.387E-05	^{129}I	7.078E-05	(4.337E-01)	^{36}Cl	2.457E-05
^{94}Nb	5.225E-05	^{246}Cm	3.563E-05	^{93}Mo	5.631E-05	(1.412E-06)	^{241}Am	2.321E-05
^{36}Cl	2.513E-05	^{36}Cl	2.511E-05	^{241}Pu	4.698E-05	(4.176E-07)	^{241}Pu	2.208E-05
^{65}Zn	1.016E-05	^{230}Th	9.608E-06	^{230}Th	3.607E-05	(1.854E-03)	^{93}Mo	6.789E-06
^{230}Th	2.715E-07	^{214}Bi	5.598E-07	^{36}Cl	3.507E-05	(7.769E-04)	^{238}Pu	3.012E-22
^{123}Sn	2.198E-09	^{214}Pb	5.598E-07	^{210}Bi	6.549E-06	(5.277E-11)	^{242}Cm	1.248E-22
^{214}Bi	7.142E-10	^{214}Po	5.598E-07	^{214}Bi	6.549E-06	(1.669E-13)		
^{214}Pb	7.142E-10	^{218}Po	5.598E-07	^{210}Pb	6.549E-06	(7.841E-08)		
^{214}Po	7.142E-10	^{226}Ra	5.598E-07	^{214}Pb	6.549E-06	(1.998E-13)		
^{218}Po	7.142E-10	^{222}Rn	5.598E-07	^{210}Po	6.549E-06	(1.457E-09)		
^{226}Ra	7.142E-10	^{210}Bi	4.539E-07	^{214}Po	6.549E-06	(2.038E-20)		
^{222}Rn	7.142E-10	^{210}Pb	4.539E-07	^{218}Po	6.549E-06	(2.317E-14)		
^{113m}In	5.417E-10	^{210}Po	4.943E-07	^{226}Ra	6.549E-06	(6.627E-06)		
^{113}Sn	5.412E-10	^{3}H	8.608E-08	^{222}Rn	6.549E-06	(4.253E-11)		
^{210}Bi	8.779E-11	^{85}Kr	8.201E-08	^{137}Cs	2.342E-08	(2.690E-10)		
^{210}Pb	8.779E-11	^{154}Eu	7.417E-10	^{137m}Ba	2.215E-08	(4.116E-17)		
^{210}Po	8.779E-11	^{60}Co	1.205E-16	^{90}Y	3.325E-09	(6.111E-15)		
^{95}Nb	1.190E-13	^{155}Eu	2.357E-18	^{90}Sr	3.324E-09	(2.316E-11)		
^{95}Zr	5.691E-14			^{244}Cm	8.123E-17	(9.749E-19)		
^{58}Co	5.873E-15			^{3}H	6.207E-25	(6.402E-29)		
^{95}Nb	3.698E-15			^{85}Kr	1.862E-27	(4.828E-30)		
^{91}Y	6.073E-16							
^{89}Sr	1.282E-18							
^{103m}Rh	5.863E-25							
^{103}Ru	5.838E-25							
TOTAL	8.961E02	TOTAL	9.632E00	TOTAL	3.914E00		TOTAL	1.061E00

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[a] This table is adapted from ORIGEN-2 calculated values presented in ORNL/TM-6008 (1977) for an 15 x 15 assembly assumed to contain 204 rods.

[b] Nuclides are listed in order of decreasing activity. Activity due to ^{235}U is not included in this table. It is estimated to be ≈3.871E-05 Ci per fuel rod.

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Table 3.3 The principal actinide ions in aqueous solutions.[a]

Ion	Stability
U^{3+}	Slowly oxidized by H_2O rapidly by air to U^{4+}
U^{4+}	Stable; slowly oxidized by air to $UO_2{}^{2+}$
$UO_2{}^{+}$	Stability greatest for pH 2-4; disproportionates to U^{4+} and $UO_2{}^{2+}$ $2UO_2{}^{+} + 4H^{+} = U^{4+} + UO_2{}^{2+} + 2H_2O$; $K = 1.7\text{x}10^6$
$UO_2{}^{2+}$	Very stable; difficult to reduce
Np^{3+}	Stable in water; oxidized by air to Np^{4+}
Np^{4+}	Stable; slowly oxidized by air to $NpO_2{}^{2+}$
$NpO_2{}^{+}$	Stable; disproportionates only in strong acid
$NpO_2{}^{2+}$	Stable; easily reduced
Pu^{3+}	Stable to water and air; easily oxidized to Pu^{4+}
Pu^{4+}	Stable in 6 M acid; disproportionates in dilute acid to $Pu^{3+} + PuO_2{}^{2+}$
$PuO_2{}^{+}$	Always disproportionates; most stable at low acidity
$PuO_2{}^{2+}$	Stable; fairly easy to reduce
Am^{3+}	Stable; difficult to oxidize
Am^{4+}	Stable in 15 M NH_4F; reduced by I
$AmO_2{}^{+}$	Disproportionates in strong acid; reduced (2% per hour) by products of its own α-radiation
$AmO_2{}^{2+}$	Reduced (4% per hour) by products from own α-radiation
Cm^{3+}	Stable; not oxidized chemically
Cm^{4+}	Stable only one hour at 25°

[a] F.A. Cotton and G. Wilkinson, 1980.

The possibility of several cationic species introduces complexity into the aqueous chemistries, particularly for U, Np, Pu, and Am. Thus, all four oxidation states of Pu can coexist in appreciable concentrations in a solution. The solution chemistries and the oxidation-reduction potentials are further complicated by the formation in the presence of ions other than perchlorate, of cationic, neutral or anionic species. Furthermore, even in solutions of low pH, hydrolysis and the formation of polymeric ions occurs. Third, there is the additional complication of disproportionation of certain ions, which is particularly dependent on the pH (Cotton and Wilkinson, 1980).

The actinides have a tendency for complex formation in aqueous solution. There are extensive series of halogen complexes, and complex ions are formed with most oxygen-containing anions such as nitrate, sulfate, carbonate, and phosphate. A large amount of data exists on complex ion formation in solution since this has been of importance in connection with solvent extraction, ion-exchange behavior and precipitation reactions involved in the technology associated with the actinides. The general tendency to complex ion formation decreases in the direction controlled by factors such as ionic size and charge, so that the order is generally $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$. For anions the order of complexing ability is generally uninegative ions, $F^- > NO_3^- > Cl^- > ClO_4^-$; binegative ions, $CO_3^{2-} > SO_4^{2-}$ (Cotton and Wilkinson, 1980).

For the radionuclide release from a repository the most likely mechanism is dissolution and further transport in the groundwater along flow paths to the accessible environment. The solubility of a radionuclide can limit the dissolution rate. Two simple dissolution models can be considered: (1) A saturation limited dissolution model, in which the rates flowing through the repository is assumed to be saturated with each waste element. This model is more conservative since it accounts for the maximum possible release; (2) A diffusion-limited dissolution model in which element saturation is assumed at the waste/water interface and dissolution is limited by diffusion of the element into water flowing past the waste.

Dissolutions of some elements such as uranium, plutonium and americium are limited by solubility. These elements can dissolve incongruently. However, dissolution rates of technetium and neptunium are not solubility limited. The dissolution rates of these elements will be limited by the dissolution rate of the bulk waste form (congruent dissolution), whether it is spent fuel, borosilicate glass, or some other solid.

Solubility is further dependent on the repository conditions such as groundwater compositions, temperature, pH, redox conditions, radiolysis effects, presence of engineered barrier materials, etc. These have been explained in greater detail in Section 2. The physiochemical parameters are particularly important because they control radionuclide solubility, speciation and sorption-- all relevant to radionuclide release and transport analysis. Due to the non-equilibrium conditions existing in a repository, it could also cause hydrolysis, disproportionation, colloid formation, gel formation, absorption and changes in the solid state species from metastable to stable form. Formation of colloids is particularly important since it could partially control radionuclide release. Depending upon the geochemical conditions, it could either be adsorbed on the packing or the host rock material, thereby reducing the radionuclide release or it could be transported through the groundwater to the accessible environment.

To evalute radionuclide release from the engineered barrier system (EBS) a large number of coupled factors need to be addressed including: changes in temperature with time, chemical interaction with materials in the repository, formation and distribution of radionuclide-bearing colloids, changes in radionuclide solubility, etc.

The purpose of the current study is to review the data on the solubilities of radionuclides from high level waste in anticipated repository waters. The formation of colloids under anticipated repository conditions also needs to be understood to evaluate the release of radionuclides by colloid transport.

3.2 Review of Individual Radionuclides

3.2.1 Americium

The two major isotopes of Americium present in the high-level waste after the containment period are: Am-241 and Am-243 which have half lives of 432 and 7.4×10^3 years respectively. According to ORIGEN-2 calculations (ORNL/TM-6008, 1977, NUREG/CR-2482, Vol. 7, 1984) Am-241 contributes the largest activity (over 60%) after the containment period of 300 years, while the activity is similar to plutonium after 1,000 years.

An earlier BNL monthly report (December 1984) reviewed the work of Edelstein and others (ONWI-399, 1983). They reported on work they have undertaken to develop a thermochemical data base for the +3 and +4 oxidation states of actinide ions, particularly the OH^- and CO_3^{-2} complexes. A second objective of their work has been the improvement of existing techniques for measurements of solution properties of these species in near neutral solutions. It should be stressed that this work is aimed at acquiring information (e.g., stability constants, hydrolysis constants, solubilities) for the purpose of modeling. As a result the "systems" studied are relatively simple and as is noted by the authors it would be misleading to "suggest that the data obtained in static laboratory measurements can alone accurately predict the behavior under dynamic field situations." Rather, these data and other similar data should be viewed as baseline information for evaluating the most important reactions and parameters, for the interpretation of other data from more complex systems and for modeling purposes.

Since it is anticipated that many nuclides would be present in solution at low concentrations an effort is being undertaken by Edelstein to improve existing methods and develop new techniques with sensitivities necessary for studying actinides in near neutral solutions.

A gross determination of actinides in solution can be accomplished by standard counting techniques. The primary drawback of such techniques are that by themselves they do not provide information on the species in solution (e.g. complexation or oxidation state), and the methods lose sensitivity rapidly in the 10^{-8} M region for those nuclides with half-lives greater than 10^5 years. Even in those cases where only gross activity is required care must be exercised in the preparation of the system and the procedures used in the analytical protocol, i.e. those steps preceding the actinide determination BNL (Monthly Letter Report, November 1984). Procedures such as solvent extraction techniques, ion exchange and electromigration, etc., can be combined with counting techniques to help supply information on speciation and complexation but have, as Edelstein noted, lead in some instances to erroneous or uncertain results.

Procedures are described and results reported for the solubilities of Am in solutions over the pH range 7 to 10. Prior to determining the solubility of Am in the pH range 7 to 10, the authors first conducted a series of experiments to determine the most favorable conditions for solubility measurements. This work involved a comparison of the concentration of Am in different supporting electrolytes, for example, pure water and solutions containing 10^{-3} M NaCl, 10^{-3} M Mg_2Cl and 0.1 M $NaClO_4$. The primary aim of this work was to arrive at conditions which would minimize radiocolloid formation and sorption of Am species on the container walls. It was found that Am is fairly stable in solutions at concentrations of 10^{-6} M or greater using 0.1 M $NaClO_4$.

Following this work, experiments were then conducted to measure the solubility of Am in near neutral solutions containing 0.1 M $NaClO_4$. Prior to summarizing the results it is interesting to note that procedural changes had to be implemented in order to make the measurements. In the initial scoping experiments with NaCl and $MgCl_2$ electrolytes, the Am-243 was first purified by cation exchange and samples of both filtered and unfiltered solutions were quantified by α-counting. When scoping studies were done using 0.1 M $NaClO_4$ supporting electrolyte α-counting could not be employed and, instead, the 75 KeV γ-ray emission of Am-243 was monitored. This procedure allowed determinations in the 10^{-9} M region with ≈10% accuracy compared to concentrations of the order of 10^{-11} M with ≈3% error.

When the solubility of Am in 0.1 M $NaClO_4$ was determined, a third counting method was used: a liquid scintillation counter. While this method is more sensitive than γ-ray counting, it requires that the daughter Np-239 be removed. While sensitivity in detection was achieved another step had to be added to the analytical protocol. Of the two standard procedures normally used, solvent extraction and ion exchange, solvent extraction was found to give "erratic" results. In addition, two different types and sizes of filters were used, and the data indicate that at higher pH (>9) differences in filter media may have led to erroneous results.

These all indicate that even with a relatively simple system (one nuclide, a single oxidation state, simple gross activity determination), care has to be taken to define the system, insure that analytical steps do not introduce large errors and insure that the techniques used to determine the property of concern are sensitive enough and that potential interferants have been eliminated or accounted for.

The results of the solubility measurements of Am in near neutral solutions are given in Table 3.4. The initial Am concentration was $\approx 10^{-5}$ M. The error in the reported Am concentrations is ≈3%. At pH 5 to 7 the concentration of Am in solution appears to remain unchanged and approximately the same as the initial concentration. From pH 8 through 10, the concentration of Am changes approximately an order of magnitude in the centrifuged, unfiltered samples, and three orders of magnitude in the centrifuged, filtered samples. It was proposed that the higher Am concentrations in unfiltered samples at pH 8-10 could be caused by finely divided $Am(OH)_3$ that is not centrifuged down at 15,000 rpm or are a result of sampling the centrifuged samples. The smaller concentration of Am in the solutions filtered through 0.4-μm filters compared to that found in solutions filtered through 0.015-μm filters may have resulted from the larger sorption area available with the larger pore size filters.

Table 3.4 Concentration of americium in solution as a function of pH. (Edelstein, et al. ONWI-399, 1983).

pH	Time (days)	Am I ($\underline{M}$) 1	Am I ($\underline{M}$) 2	Am I ($\underline{M}$) 3	Am II ($\underline{M}$) 1	Am II ($\underline{M}$) 2	Am II ($\underline{M}$) 3
4.95 ± 0.05	4	0.954×10^{-5}	0.964×10^{-5}		0.9451×10^{-5}	0.913×10^{-5}	
5.90 ± 0.15	5	1.020×10^{-5}	1.048×10^{-5}		1.059×10^{-5}	1.042×10^{-5}	
6.85 ± 0.20	7	0.873×10^{-5}	0.912×10^{-5}		0.921×10^{-5}	0.936×10^{-5}	
7.90 ± 0.15	23	3.757×10^{-6}	3.393×10^{-6}	2.131×10^{-6}	5.715×10^{-6}	5.322×10^{-6}	3.975×10^{-6}
8.95 ± 0.10	21	1.699×10^{-7}	1.140×10^{-8}	2.362×10^{-8}	7.700×10^{-8}	1.288×10^{-8}	1.297×10^{-8}
10.00 ± 0.05	12	1.595×10^{-7}	1.750×10^{-9}	5.040×10^{-9}	7.716×10^{-8}	1.698×10^{-9}	4.394×10^{-9}

1 - centrifugation; 2 - centrifugation plus 0.40 μm filtration; 3 - centrifugation plus 0.015 μm filtration.

Initial Am concentration = $1.023 \pm 0.031 \times 10^{-5}$ $\underline{M}$.

The measurements of the solubility of Am in near neutral solutions (≈pH 7) approach equilibrium or steady state concentrations from a condition of oversaturation, i.e. the basic assumption is made that the solubility of $Am(OH)_3$ in pH >7 water is less than 10^{-6} M. A similar approach was adopted by Silva and Yee (LBL-14696, 1982). In neither case was equilibrium approached from an undersaturated condition.

Table 3.5 compares the solubilities measured by Silva and Yee with those reported by Edelstein. There are differences in the way in which these two determinations of solubility were made. The solubility determined by Edelstein was made with an initial concentration of 10^{-5} M in Am while that used by Silva and Yee was 10^{-7} M, equilibration times are not always identical, the filters differed in pore size, and the supporting electrolytes differed in both nature and concentration.

Table 3.5 Solubilities (M) of americium.

pH	C_o[1]	Cuf[2] (Edelstein)	Cuf[2] (Silva and Yee	Cf[3,4] (Edelstein)	Cf[4] (Silva and Yee)
6.85	1E-5	8.7E-6			
		9.2E-6			
7.0	1.6E-6			1.4E-6	
7.9	1E-5	3.8E-6		3.4E-6(2.1E-6)	
		5.7E-6		5.3E-6(4E-6)	
8.6	1.6E-6			4.2E-7	
8.77	1E-7		3.7E-8		3.8E-8
8.91	1E-7		3.5E-8		4E-8
8.95	1E-5	1.7E-7		1.1E-8(2.4E-8)	
		7.7E-8		1.3E-8(1.3E-8)	
9.67[5]	1E-7		6.1E-8		5.9E-8
9.76[5]	1E-7		6.8E-8		6.6E-8
9.8	1.6E-6			4.5E-9	
10.0	1E-5	1.6E-7		1.8E-9(5E-9)	
		7.7E-8		1.7E-9(4.4E-9)	

[1] C_o is the initial concentration of the solution.

[2] Cuf is the concentration of the unfiltered solution, centrifuged at 15,000 rpm.

[3] 0.4 μm Gilman filter; parentheses indicates solution concentration after filtration through the 0.015 μm filter.

[4] 0.2 μm Gilman filter.

[5] Simulated basalt waters.

At pH ≈8.9 the solubilities determined after centrifugation of the sample agree within a factor of ≈5. Over the entire range of 7 to 10 including the solubility determined in basalt water, the solubility as determined from the centrifuged, unfiltered samples varies from $\approx 10^{-5}$ to 10^{-7} M. The discrepancies which occur are in those values of the solubility determined from filtered samples and between filtered and centrifuged samples. The data of Silva and Yee at pH ≈8.7 are almost two orders of magnitude lower than that of Edelstein. The difference decreases at higher pH. Approximately a two-order of magnitude difference then exists between filtered versus centrifuged samples in the narrow pH region of 8.7 to 9.0.

Edelstein and others have argued that to correctly determine the solubility initial concentrations of less than 10^{-5} M should not be used since this leads to losses due to sorption and colloid formation. At higher pH and lower concentrations the effects are even worse. This may explain some of the differences between the work of Edelstein and that of Silva and Yee but does not fully reconcile the differences at pH 8 to 9. It is interesting to note that in the work of Silva and Yee there are only small differences between filtered, centrifuged and gravity settled samples whereas at high pH (9.8 to 10) almost two orders of magnitude difference exist in the data reported by Edelstein. Since the conditions used in these two works are not identical and since "equilibrium" was not approached from both directions, it is not clear whether the concentrations determined truly represent the solubility limit of Am in this pH range. In addition, it would appear that differences in the analytical procedures and experimental conditions may have introduced uncertainties as large as two orders of magnitude in the determined concentrations.

For evaluating the source term at the package surface this data merely indicates order of magnitude variations that could arise as the pH changes. It is not clear how useful the data would be for modeling since "equilibrium" has not been demonstrated and the experimental differences may have introduced uncertainties.

Wood and Ray (PNL-SA-9549, 1981) have reported the Am solubility of Am-contaminated sediments in air-equilibrated solutions. Even though this system is entirely different from what is expected in a high level waste repository, it would be of interest to know the solubility values generated from this study. An equation was derived for solubility between the pH range 4 to 8:

$$\text{Am solubility (M)} = 7.6 \times 10^{-(5+\text{pH})}$$

At pH 7.0, the solubility value is $7.6\text{x}10^{-12}$ M.

This value is much lower than the value of about 10^{-6} M reported by Edelstein, et al.

3.2.1.1 Tabulation of Solubility Data for Americium

Many of the Americium solubility values reported in the literature are compiled in Table 3.6. All these values are for room temperature.

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The Eh does not have much effect on the solubility since under both oxidizing and reducing conditions, the same solubility values are obtained. (See values compiled by Krauskopf given in reference, Pigford, et al.).

However, the effect of pH is not well understood. For example the values compiled by Krauskopf shows that Am solubility decreases with increasing pH, and reported a value of 10^{-8} ppm at pH 9.0, whereas the values given by Edelstein, et al. and Silva and Yee are between 0.9 and 4×10^{-2} ppm at pH 8 to 10. Although the test conditions used in both cases are different, the solubility values are apparently too far apart to be explained on this basis.

Table 3.6 Solubility of americium.

Reference	Solubility (ppm)	Conditions
Table compiled by Krauskopf* (Ref. Pigford, et al., 1983)	10^{-4}	not specified
	10^{-8}	pH=9.0 (for both oxidizing and reducing)
	10^{-5}	pH=6.0 (for both oxidizing and reducing)
Early (1983)	4.8×10^{-3}	Reference Grande Ronde groundwater under reducing conditions Eh=-0.3V.
Salter (1982)	2.4×10^{-5}	Basalt groundwater under reducing conditions
Ogard and Kerrisk (Ref. in J.F. Kerrisk, LA-UR-84-3054, 1984)	2.4×10^{-3}	Tuff groundwater (Yucca Mountain) under oxiding conditions
Edelstein, et al. (ONWI-399, LBL-14325, 1983)	0.9 4.1×10^{-2} 3.9×10^{-2}	pH= 7.9 pH= 9 pH=10
Silva and Yee (LBL-14696, 1982)	9.0×10^{-3} to 1.6×10^{-2}	pH=8.8 to 9.7
Wood and Ray (PNL-SA-9549, 1981)	1.8×10^{-6}	pH=7.0 Am contaminated sediments

*(There are concerns on the solubility data compiled by Krauskopf for various radionuclides since the original references could not be located in many cases. However, these are reported here, since they have been used in DOE calculations.)

3.2.2 Plutonium

After the containment period of 300 to 1000 years, plutonium will be present as Pu-239 and Pu-240, which have half-life values of 2.41×10^4 and 6.57×10^3 years, respectively. Plutonium solution chemistry is complicated, since plutonium can exist in four oxidation states. Several studies have been conducted for plutonium release rates and solubilities in different groundwaters, as well as deionized water. This section reviews a few of these investigations to evaluate the testing procedures and the available data for plutonium release and solubility in repository groundwaters.

Plutonium-239 solubility was reviewed in a report on the "Defense High Level Waste Leaching Mechanism Program," (PNL-5157, 1984). In addition to plutonium, dissolution behavior of uranium, neptunium and technetium and the effect of Eh as a leaching variable were also reviewed. The borosilicate glass used in the tests was doped with Pu-239. However, the dopant level was 0.03 wt % PuO_2, about 10 times higher than in a real defense waste glass. This higher dopant level was maintained for analytical reasons. This could give a substantially different release rate than the actual case. However, the results of this study may give a conservative estimate of the Pu release, since it assures that actinide concentration measured in solution was not limited by available inventory because of the low waste form surface-area to solution-volume ratio used in the tests.

Four leachants were investigated: deionized water, a simulated basaltic groundwater, a Permian Basin brine, and tuff groundwater obtained from Well J-13 near the Yucca Mountain site. The composition and initial pH values are listed in Table 3.7. All tests were conducted using the standard MCC-1 test. The tests were conducted with or without an iron coupon present. Some of the leach test data obtained for one of the solutions, viz., brine, are shown in Fig. 3.1(a) and 3.1(b).

Table 3.8 summarizes the total release of Pu-239 in each solution and the relative percentage of that total associated with colloids, true solution (filtered), the iron coupon, and the acid strip on the vessel walls. The latter two give Pu concentrations absorbed on the iron coupon and vessel walls.

When iron is present, the dominant form of Pu-239 in the solution is a filterable, colloidal Pu-239. The colloids may be true Pu-239 colloids, pseudo colloids (i.e., Pu-239 sorbed on to a precipitate), or a mixture. Depending on the size, charge, mobility, and subsequent interactions of these Pu-239 colloids, the interactive effect of iron on the waste glass could be beneficial. There is evidence from Table 3.8 that the truly soluble portion of Pu-239 released from the glass is lower in the presence of iron for all ground waters. This may be related to the local reducing conditions produced by corrosion of iron by water.

Table 3.7 Groundwater compositions used in tests on defense waste reference glass (DWRG)

Constituents	Amount Present (mg/L)		
	Tuff Water	Basalt Water	Salt Brine
Ca	13.2	1.3	1,560
K	5.0	1.9	39
Mg	2.1	0.04	134
Na	47.0	263.0	123,000
Sr	0.004	--	35
Si	30.2	56.0	--
Zn	--	--	7.8
F^-	2.1	37.0	1.1
Cl^-	7.4	148.0	191,000
CO_3^{2-}	0.0	27.0	0.0
HCO_3^-	120.0	70.0	30
SO_4^{2-}	18.3	109.0	3,200
NO_3^-	8.0	1.3	--
pH	7.5-8.5	9.0-10.0	6.7-7.7

Table 3.8 Systematics of Pu-239 release after 56-day duration[(a)]

System	Total Release (ppb)	Colloidal	Filtered	Iron	Acid Strip
Brine	0.43 ± 0.05	10%	65%	-	25%
Brine + Iron	2.05 ± 0.05	80%	<1%	5%	15%
Basalt Water	0.14 ± 0.03	15%	50%	-	35%
Basalt Water + Iron	4.85 ± 0.15	90%	<1%	5%	5%
D.I. Water	1.00 ± 0.05	← 60% →		-	40%
D.I. Water + Iron	16.3 ± 1.5	70%	<1%	5%	25%

(a) Leach tests at 90°C.

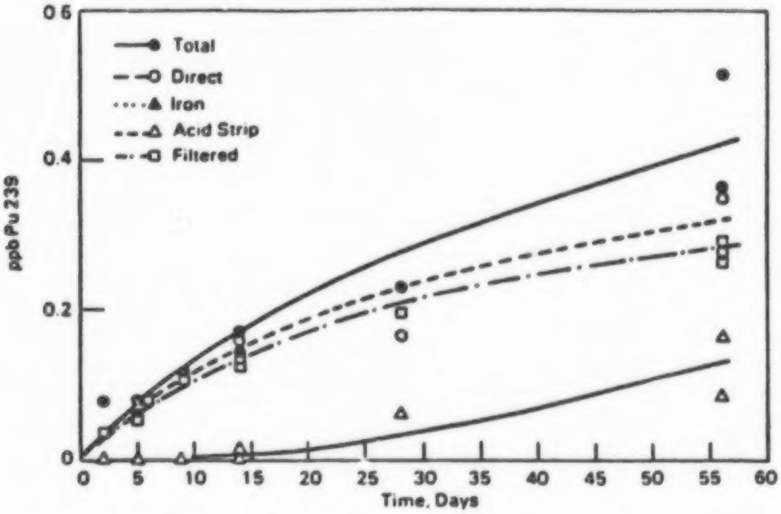

Figure 3.1a Plutonium-239 release in brine solution (90°C).

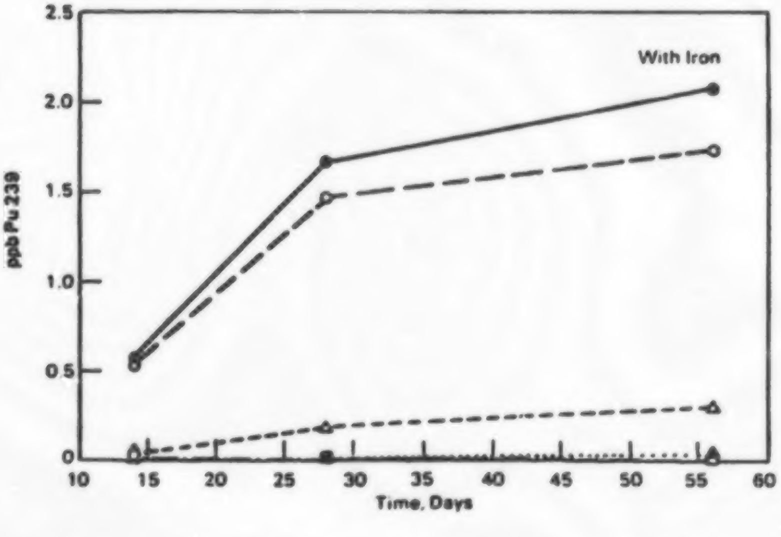

Figure 3.1b Plutonium-239 release in brine solution with iron coupon present (90°C).

The total plutonium released from the test sample increased in the presence of iron by a factor of 5 in brine, by a factor of about 35 in basalt water, and by a factor of 16 in deionized water.

In all the experiments, the total amount of Pu-239 released was still increasing, even at the end of the 56-day period. This shows that the solubility limit had not been reached.

Wood and Rai (PNL-SA-?549) calculated the fractional release rate for actinides such as U, Np, Pu and Am from waste forms (borosilicate glass or spent fuel). They gave the following equation:

$$\text{Fractional Release Rate} = \frac{SV}{A}$$

S: Solubility of actinide in M.
V: Volume of water passing through repository per unit volume
A: Total amount (moles) of element in waste.

The maximum fractional release rate at which an element can be released from a repository is obtained by assuming that the groundwater is completely saturated by the element of interest which has limited solubility and that the concentration is controlled by the solubility of the solids in the waste form which has unlimited solubility.

From experimental data, Wood and Rai devised the following equation for crystalline $PuO_2(c)$ solubility in air-equilibrated dilute salt solution ($0.0015M\ CaCl_2$):

$$\text{Solubility (M)} = 1.26 \times 10^{-(4 + 0.64\ \text{pH})}$$

$$\text{pH} = 3 \text{ to } 8$$

At pH = 7, the $PuO_2(c)$ solubility was calculated to be 4×10^{-9} M with a fractional release rate of 3×10^{-9}/year, assuming a groundwater flow rate of 2×10^{6} L/year.

Bibler et al. (UCRL-91252) studied the leaching of Savannah River Plant (SRP) nuclear waste glass containing either simulated or actual radioactive waste at 90°C under conditions simulating a saturated tuff repository environment. A saturated environment represents a possible worst case, since the potential repository horizon being investigated by NNWSI is in the unsaturated zone and the amount of water will be limited. The leach vessels were fabricated from tuff and actual tuff groundwater was used. Thus, the glass was leached only in the presence of those materials (including the Type 304L stainless steel canister material) that would be in the actual repository. Tests were performed for time periods up to 6 months at a SA/V ratio of 100 m^{-1}.

During the leach tests, the pH of the tuff groundwater changed from its pre-test value of 7.4. to 7.9. When tuff rock was present, the changes were small, indicating that tuff rock buffered the pH. Also, the changes in the presence of Type 304L stainless steel were not significantly different from those in its absence.

Leach results are presented as normalized mass losses (NL_i) based on the respective elements for each time period.

$$NL_i = \frac{N_i}{SA \times X_i}$$

where NL_i = mass of glass dissolved per unit area based on species i.
N_i = total amount of species i measured in the solution
SA = surface area of the glass
X_i = mass fraction of i in the glass

In addition to Pu-238, the leach results were reported for Li, B, Cs-137 and Sr-90. Figure 3.2 shows normalized mass loss for actual radioactive glass containing Pu-238 in the presence and absence of tuff. Single tests were performed for each time when tuff was present. Duplicate and triplicate tests were performed in the absence of tuff. The error bars show wide variations for the normalized release of Pu-238.

Bates, et al. (1983) conducted extended leach studies of actinide-doped SRL-131 glass in D.I.W. at 90°C. They reported normalized leach results of several actinides, including Pu-239. Their results for Pu-239 are plotted in the same graph shown in Figure 3.2. Though the leaching solutions and the isotopes are different in both cases, it is desirable to make a comparison of the two sets of data. The authors believe that the large variation in the SRP glass results when tuff is absent may be due to experimental error. These data also have large uncertainty as shown in the figure.

The normalized release rate for Pu-239 was higher in deionized water compared to Pu-238 release in J-13 water with tuff present. It is interesting to note that the Pu-238 concentration decreased slightly in the latter part of the test with tuff present. Therefore, the presence of tuff is beneficial in decreasing the concentration of Pu-238 in the leachant during the experiment. The concentration of Pu-238 at the conclusion of the test was as low as 0.006 ppb.

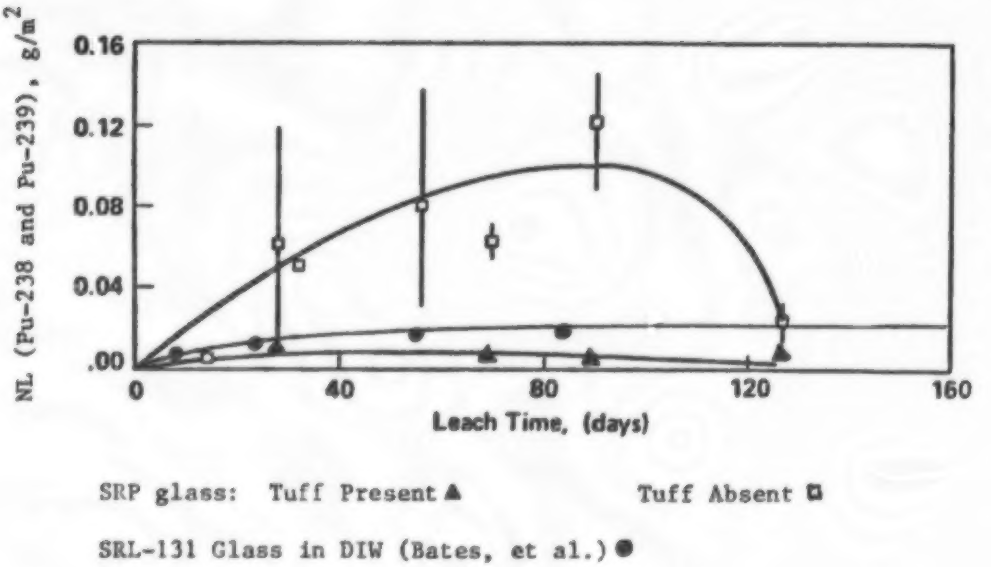

Figure 3.2 Normalized mass losses for Pu-238 and Pu-239.

Cleveland et al. (1983) studied plutonium speciation in selected basalt, granite, shale, and tuff groundwaters. Since granite and shale are not of interest in the present study, these are not reviewed here. The basalt and tuff groundwaters used in this study have compositions as shown in Table 3.9.

In the experimental study, small aliquots of stock solution containing ≈ 10^{-5}M Pu-239 (of known oxidation state) in 0.5M perchloric acid was added to measured volumes of basalt and tuff groundwaters and deionized water. In the deionized water runs, the pH was adjusted to 8.5 with dilute NaOH after addition of the stock solution. The resulting plutonium concentration in the waters was ≈ 10^{-9}M. Samples were taken from agitated solutions at 1,3,7,17 and 30 days and were analyzed for total plutonium, Pu(III), Pu(IV), Pu(V) and Pu(VI). To determine the effect of the initial oxidation state of the added plutonium on the final speciation, two series of experiments were run, one starting with a stock solution containing primarily Pu(III) and Pu(IV), and one utilizing a solution containing primarily Pu(V) and Pu(VI). To evaluate the effect of temperature, experiments were conducted at 25°C and 90°C. All experiments were run in duplicate, and the values shown are the average of the two runs. The accuracy was estimated to be within 15%.

Table 3.9 Groundwater Compositions (mg/L).

Solute	Tuff	Basalt
Alkalinity (as $CaCo_3$)	98	146
Calcium	10	<0.1
Iron	0.007	0.3
Magnesium	3	<1
Manganese	0.001	0.005
Potassium	4.2	3.0
Sodium	50	300
Strontium	0.05	0.01
Silica	70	100
Chloride	7	140
Fluoride	2.3	52
Phosphate	<0.01	0.1
Sulfate	19	75
pH	7.8	9.3

The results of the speciation experiments were reported as bar graphs of soluble and insoluble plutonium species in different solutions. To make a graphical comparison, the percentages of soluble plutonium in the solution are tabulated in Tables 3.10 and 3.11 and are plotted in Figures 3.3, 3.4 and 3.5.

Plutonium was most soluble in the basalt groundwater. In deionized water at 90°C, after 30 days, most of the plutonium was still in the solution, when initially solution containing low oxidation state Pu (i.e., Pu(III) and Pu(IV)) was used. When solution containing high oxidation state Pu (i.e., Pu(V) and Pu(VI)) was used, most of the Pu was precipitated.

In the case of tuff groundwater, more than half the plutonium added formed insoluble species within 30 days.

Among the various factors causing differences in the solubilization, it was found that the higher the sulfate concentration in solution, the less the plutonium solubility. Similarly, the presence of fluoride can enhance plutonium solubility. The combined effect of sulfate and fluoride ions varied between groundwaters and deionized water.

Table 3.10 Plutonium concentration at 25°C.

Time (Days)	Low Oxidation State Pu Added			High Oxidation State Pu Added		
	Soluble Pu (% of Init. Conc.)			Soluble Pu (% of Init. Conc.)		
	Basalt	D.I.W.	Tuff	Basalt	D.I.W.	Tuff
0	100	100	100	100	100	100
1	88	30	100	99	100	90
3	86	18	86	100	86	77
7	83	11	55	94	100	90
17	90	9	56	98	93	79
30	100	4	44	98	96	84

Table 3.11 Plutonium concentration at 90°C.

Time (Days)	Low Oxidation State Pu Added			High Oxidation State Pu Added		
	Soluble Pu (% of Init. Conc.)			Soluble Pu (% of Init. Conc.)		
	Basalt	D.I.W.	Tuff	Basalt	D.I.W.	Tuff
0	100	100	100	100	100	100
1	84	92	60	95	80	100
3	96	93	66	94	85	96
7	72	97	57	82	74	78
17	67	88	17	98	79	20
30	68	85	6	78	26	12

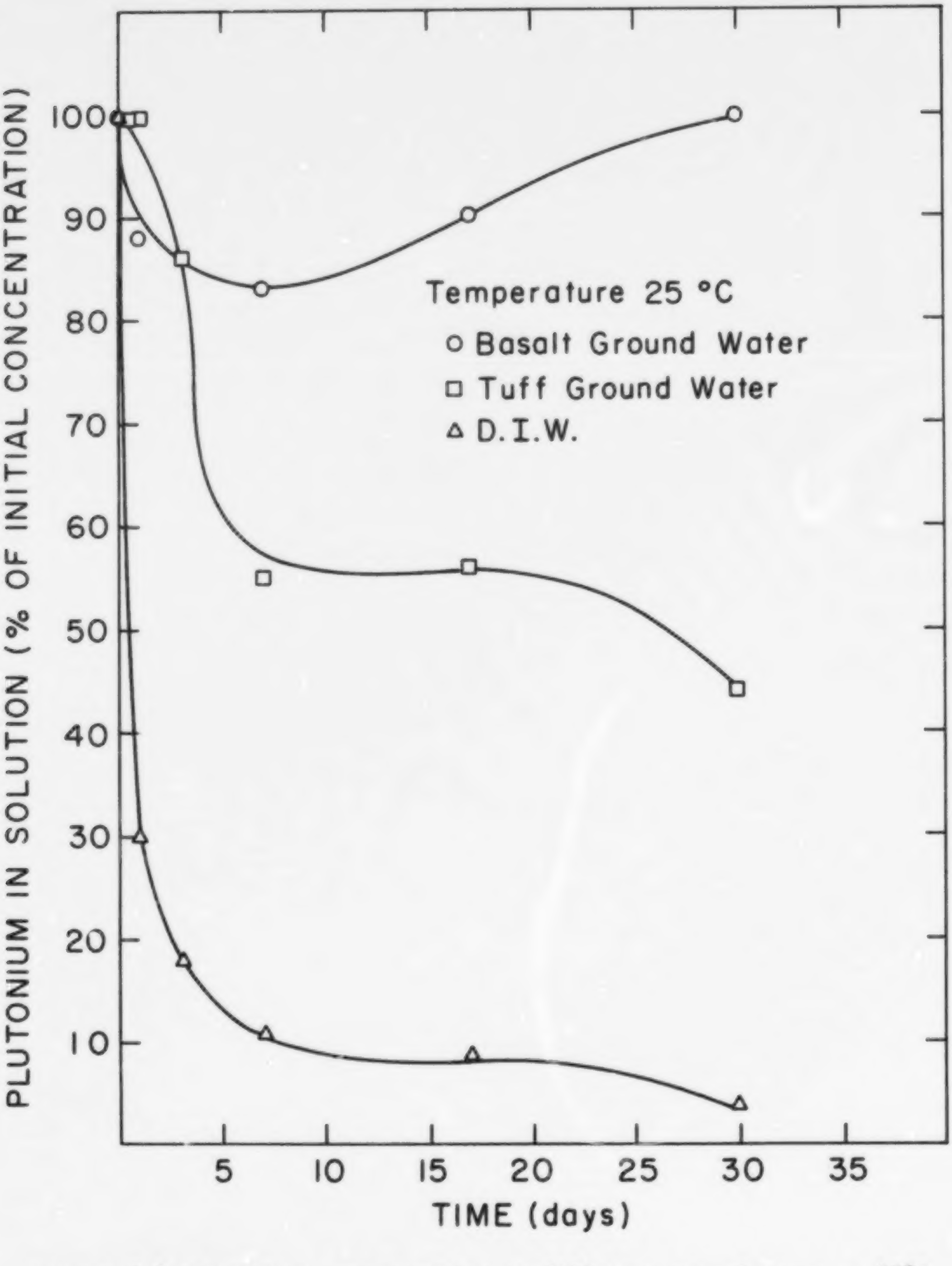

Figure 3.3 Plutonium concentration in different groundwaters at 25°C (solution containing low oxidation state Pu was added initially).

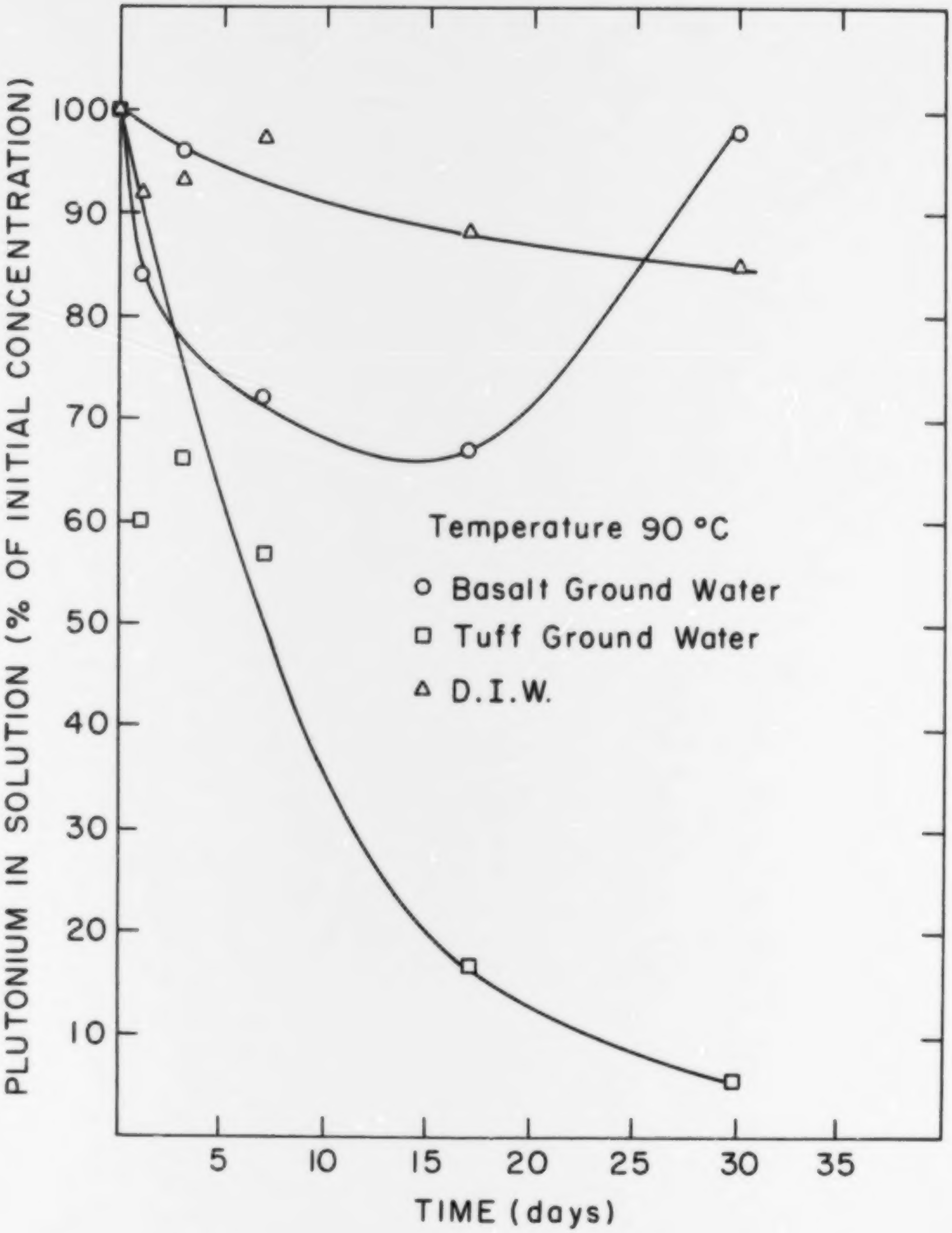

Figure 3.4 Plutonium concentration in different groundwaters at 90°C (solution containing low oxidation state Pu was added initially).

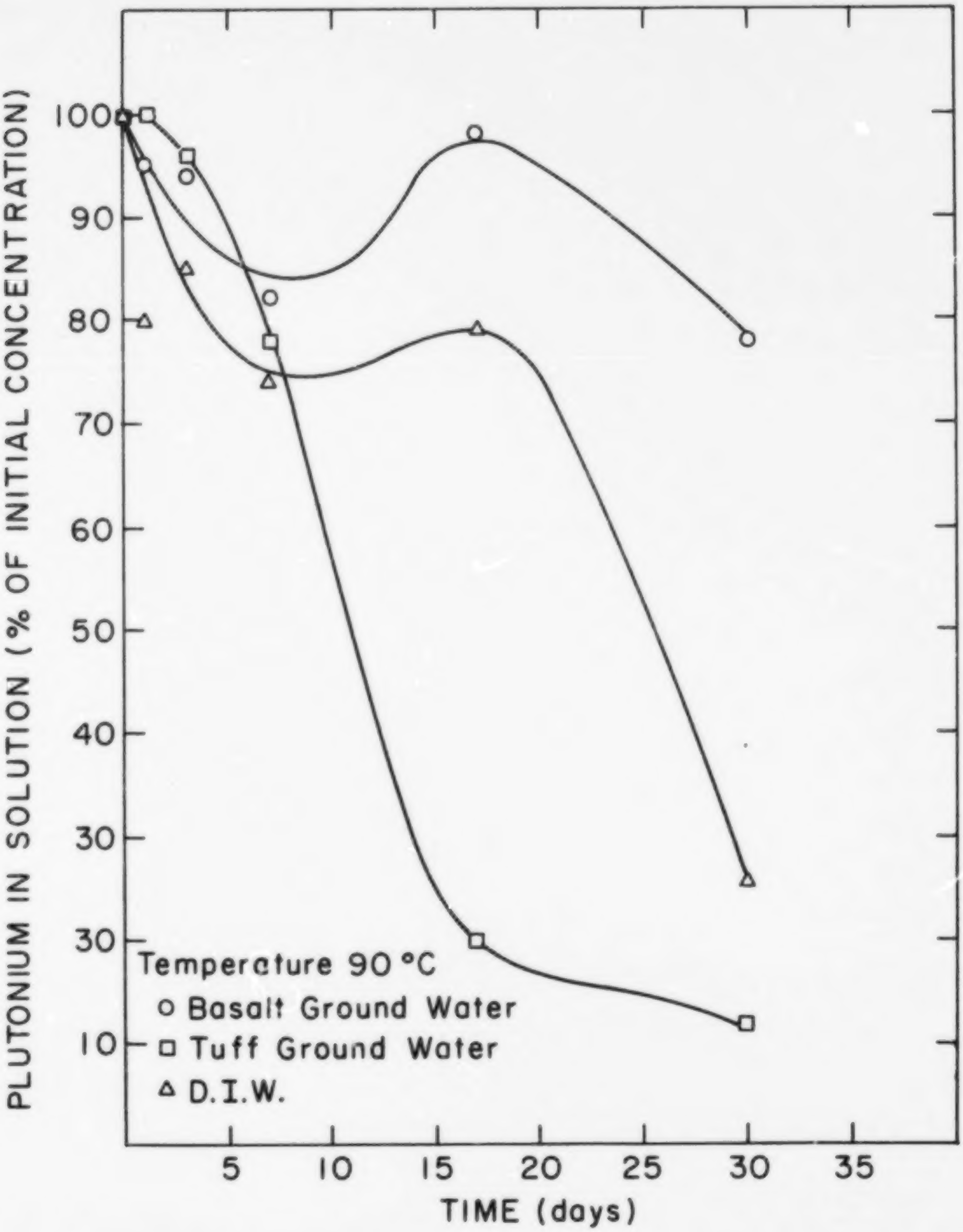

Figure 3.5 Plutonium concentration in different groundwaters (solution containing high oxidation state Pu was added initially).

Cleveland's work shows the importance of using actual groundwaters in the laboratory investigations instead of deionized or distilled water. This study should be further extended with higher initial concentrations of plutonium in the solution and in the presence of container and packing materials to evaluate synergistic effects. Also, tests should be conducted for longer times to ensure that equilibrium is achieved.

This investigation further confirms that the solubility data in deionized water need not be the most conservative solubility data. Depending on the composition, the solubility of radionuclides could be more or it could be less in the groundwaters compared to deionized water.

3.2.2.1 Tabulation of Solubility Data for Plutonium

Some of the solubility data reported in the literature are compiled in Table 3.12. Most of these values are for 25°C. There is a wide variation in the solubility values from 10^{-3} ppm to 10^{-7} ppm because of differences in test conditions. The effect of Eh on the solubility of Pu is not well understood since the solubility values vary under similar oxidizing or reducing conditions.

Table 3.12 Solubility of plutonium

Reference	Solubility (ppm)	Conditions
Table compiled by Krauskopf (Ref. by Pigford, et al., 1983)	10^{-3}	Not specified
	10^{-5}	Reducing; pH = 9 (Eh = -0.2V)
	10^{-4}	Reducing; pH = 6 (Eh = -0.2V)
	10^{-5}	Oxidizing; pH = 9 (Eh = +0.2V)
	10^{-3}	Oxidizing; pH = 6 (Eh = +0.2V)
Early (1982) (Ref. in ORNL/TM-9191/V2, 1984)	10^{-7}	Groundwater under reducing conditions (calculated)
Salter (1982)	2.4×10^{-7}	Basalt groundwater under reducing conditions
Ogard and Kerrisk (Ref. in J. F. Kerrisk, LA-UR-84-3054, 1984)	4.3×10^{-4}	Tuff groundwater (Yucca Mountain) under oxidizing conditions
Wood and Rai (PNL-SA-9549, 1981)	2.4×10^{-7}	Pu-doped glass in groundwater under oxidizing conditions; pH = 7. (Eh = 0.29V)
	9.6×10^{-7}	PuO_2(c) in air equilibrated groundwater

3.2.3 Neptunium

Neptunium is present in significant quantities in high level waste. However, like Americium, there has been little work on its solubility in repository groundwaters. The few solubility studies have been at room temperature but some have been carried out at 90°C and 200°C. These are reviewed below.

Krupka, et al, (PNL-SA-1984) reported solubility data for Np (IV) hydrous oxide at ambient temperature in carbonate-free near-neutral to alkaline solutions. To understand the effect of flouride complexation on the solubility of Np (IV) hydrous oxide, the water contained 100 ppm F^-. Some tests were maintained under reducing conditions by adding either powdered metallic Fe or an alkaline solution of 0.05M $Na_2S_2O_4$. Np (IV) was added from a concentrated Np (IV) stock solution in HCl. The pH was adjusted to >6 using carbonate - free NaOH solution, which resulted in the precipitation of Np (IV) hydrous oxide. Therefore, the solubility limit was approached from an over-saturation condition. The Np (IV) hydrous oxide suspensions were equilibrated at ambient temperature for about 7 days in a nitrogen - filled, controlled atmosphere chamber. The pH and Eh were measured for each experiment. The suspensions were sampled and the 1.8 - nm filtered aliquots were analyzed for Np concentration and oxidation states. Solids separated from some of the Np suspensions were analyzed by X-ray diffraction.

The measured Np concentrations in the presence of 100 ppm total F^- were all at the detection limit for the scintillation counter used (7.7×10^{-9} M).

In a previous study by Rai and Ryan (PNL-SA-12096), similar results were obtained in the absence of F^-. X-ray diffraction showed no crystalline phases. This investigation showed that high F^- concentrations (e.g. 100 ppm) in near neutral to alkaline solutions do not measurably increase the solubility of Np (IV) hydrous oxide.

In evaluating the testing procedures, the concentration of Np (IV) in the solution is near the detection limit, so filtering the solution might cause some inaccuracies in the concentration values. Instead of filtration, the sample could have been centrifuged. Secondly, it is not certain whether equilibrium was reached in 7 days.

The study is useful, since it measured the solubility from oversaturation. However, the value of the data is limited by the "system" studied. The experimental conditions used in this test are not close to anticipated repository conditions.

Strickert, et al. (1983) studied the effect of aging on the solubility and crystallinity of Np (IV) hydrous oxide in aqueous suspensions with pH values ranging from 4 to 12. A stock solution of ^{237}Np (IV) was prepared in 1 M HCl. Aliquots of the Np (IV) stock solution were adjusted with NaOH to an approximte pH value of 12 to precipitate the brown Np (IV) hydrous oxide. These suspensions were centrifuged and the supernatants were discarded. The

Np solids were resuspended and the pH of the suspensions were adjusted with HCl or NaOH to pH values between 4 and 12. The experiments were conducted in an argon atmosphere control chamber for up to 270 days. At the conclusion of the experiments, the solutions were centrifuged and then filtered through a 1.8 nm pore-size filter. The solutions were alpha counted using liquid scintillaion techniques. The Np oxidation state was analyzed by a thenoyltrifluoroacetone extraction procedure. Major cations in the solution were determined by inductively coupled plasma spectometry analyses. A small portion of the solids were analyzed by X-ray diffraction techniques.

The Np solution concentrations are plotted as a function of measured pe (defined as - $\log_{10}$ of the electron activity) and this is shown in Figure 3.6.

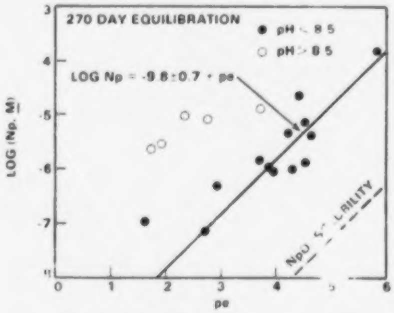

Figure 3.6 Log Np concentrations in filtered solutions contacting Np (IV) hydrous oxide as a function of pe. Solid lines are fitted to data from pH<8.5 solutions. Dashed line is based on NpO_2 solubility data from previous work. (PNL-SA-10590, 1982). (Reproduced from Strickert, et al.)

In the experiment, Np solution concentration reached steady-state values within 70 days. With the aging of the Np solid phase, the solubility also decreases slightly. In all the pH ranges, the solubility ranged between 10^{-7} and 10^{-5} M. The solids after the experiment, analyzed using X-ray diffraction, showed $NpO_2(c)$. Figure 3.7 shows a plot of log of solubility product constant (K°) for the reaction,

$$NpO_2 \cdot x\,H_2O = NpO_2^+ + e^- + x\,H_2O$$

With equilibration time, log K decreases. However, from the figure, it is not clear whether the solubility will decrease further with time. Also, the authors have plotted this curve assuming that $NpO_2 \cdot x\,H_2O$ is the solid present in the later part of the experiment. However, their own study showed that within one month, the solids in suspension included $NpO_2(c)$.

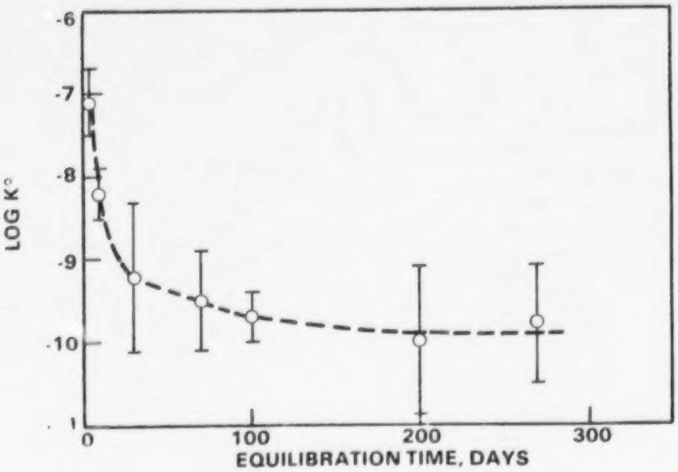

Figure 3.7 Apparent log K° for the reaction $NpO_2 \cdot x\ H_2O = NpO_2^{+} + e + x\ H_2O$, for various equilibration times. Error bars based on fitted intercept values. (Reproduced from Strickert, et al.)

It is not clear, whether all solids are converted to NpO_2 (c). The presence of amorphous $NpO_2 \cdot x\ H_2O$ in the solids after the experiment of course cannot be identified from the X-ray diffraction pattern. Also the higher pH experiments showed solids of higher oxidation states such as Np (V and VI). Therefore, in the later part of the experiments, there are several equilibrium reactions involving different Np solids and the aqueous phase, rather than just one reaction mentioned above. Based on this argument, we could question the validity of the solubility product values given for $NpO_2 \cdot x\ H_2O$.

Cleveland, et al. (1983) studied neptunium speciation in groundwaters associated with rock types proposed as possible hosts for nuclear waste repositories. The groundwater compositions and the experimental procedure are explained in greater detail in the section on plutonium. Sufficient Np-237 in 0.5 M to 1.0 M $HClO_4$ solution was added to achieve a concentration of approximately 10^{-8}M in the waters. After equilibration, the solution filtered through a 0.05-µm filter, was analyzed for Np (III, IV and V).

To assess the effect of initial oxidation state, separate experiments were conducted using reduced [primarily Np (IV)] and oxidized [primarily Np (V)] neptunium. To determine the effect of temperature, experiments were conducted at 25°C and 90°C.

The neptunium speciation results are shown in Table 3.13 and Table 3.14. For the groundwaters containing added Np(V) (Table 3.13), essentially all neptunium remained in solution in this oxidation state at both temperatures.

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Table 3.13 Percentages of neptunium in solution at various time [Np(V) was the only oxidation state detected in solution] after addition as Np(V); 100 percent of the neptunium was present initially as Np(V). Estimated uncertainty, ± 15 percent.

Groundwater	1 day		3 days		7 days		17 days		30 days	
	25°C	90°C	25°C	90°C	25°C	90°C	25°C	90°C	25°C	90°C
Basalt	74	81	83	83	79	90	86	87	89	81
Tuff	91	88	93	93	95	77	85	77	95	79
Deionized	88	88	80	89	88	89	94	92	88	91

Reproduced from Cleveland, et al., 1983.

Table 3.14 Percentages of neptunium in solution at various times [Np(V) was the only oxidation state detected, except for the two parenthetical values, which are percentages of Np(IV)] after addition as Np(IV);>99 percent of the neptunium was present initially as Np(IV). Estimated uncertainty, ± 15 percent.

Groundwater	1 day		3 days		7 day		17 days		30 days	
	25°C	90°C	25°C	90°C	25°C	9 °C	25°C	90°C	25°C	90°C
Basalt	80(23)	95(10)	96	72	87	94	90	94	79	88
Tuff	80	87	91	95	88	91	85	100	87	12
Deionized	93	98	85	86	87	95	85	100	76	96

Reproduced from Cleveland, et al., 1983.

When neptunium was added in the Np(IV) state, most of it was converted to Np(V). In tuff groundwater at 90°C, the concentration decreased considerably due to the formation of insoluble species. Basaltic groundwater contains flouride ions, however, it did not have much effect since the results were similar to deionized water. In an earlier study on plutonium speciation by the same authors, it was found that, flouride ions enhanced Pu solubility.

Schramke, et al. (1984) carried out hydrothermal experiments on Np-237 and Pu-239 doped PNL 76-68 glass, synthetic basalt groundwater, basalt and cast steel. The experiments were conducted in Dickson-type rocking autoclaves at 200°C and 30 MPa, with an initial fluid to solid ratio of 10:1. The ground and sieved glass used in the experiments had a Np content of 2 mg/g glass. The cast steel as well as the basalt were in fine particle form. The synthetic groundwater used had an initial pH of 9.74.

The four experiments conducted contained the starting materials, glass and groundwater; glass, basalt, and groundwater; glass, steel and groundwater; and glass, steel, basalt, and groundwater. Each experiment ran for three months, and fluid samples were withdrawn at approximately two-week intervals. After a fluid sample was taken, it was split, filtered and analyzed. Unfiltered, 4,000Å filtered, and 18Å filtered fluids were analyzed for Np-237.The 4,000Å filtration step should remove particulate matter from the fluid, and 18Å filtration step should, in turn, remove colloidal material.

The concentrations of Np-237 in the unfiltered solution samples are shown in Figure 3.8. It is seen that the experiments that contained basalt had higher concentrations of Np in solution than the experiments without basalt. In all four experiments, the quantities of the actinide dopants in the solutions from the experiments were much smaller than would be predicted, based on the amount of glass dissolved. Therefore, after release from the glass, the actinides were removed from solution by precipitation or adsorption.

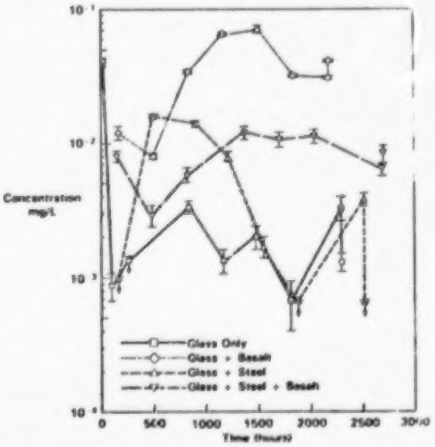

Figure 3.8 Concentrations of Np-237 in unfiltered samples from the four experiments. Arrows on the data points indicate analyses that were less than the plotted value. (Schramke, 1984).

The concentration of colloidally associated Np-237 obtained by subtracting the 18Å filtered solution data from the 4,000Å filtered solution data are plotted in Figure 3.9. The highest concentrations of colloidally associated Np-237 were observed in the experiment with glass, basalt and groundwater.

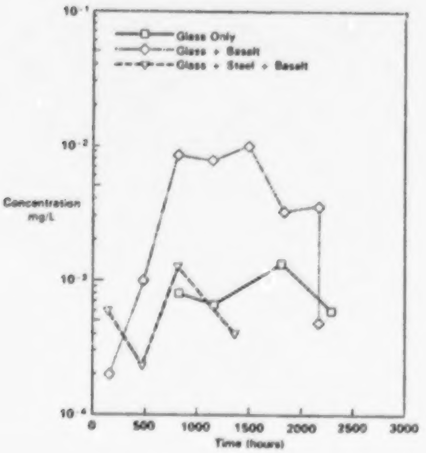

Figure 3.9 Concentrations of colloidally associated Np-237 in the solutions of the experiments. No colloidally associated Np-237 was detected in the solutions from the glass, steel, and groundwater experiment. (Schramke, 1984).

No colloidally associated Np-237 was detected in the experiment with glass, steel and groundwater. In the other experiments, glass and groundwater as well as glass, steel, basalt, and groundwater, colloidally associated Np-237 was present in amounts approximately equal to the detection limit of 10^{-3} mg/L.

This investigation is useful since it shows the formation of colloids containing Np especially when basalt is present in the test. There is some uncertainty in the data obtained here. The pH of the solution sample was measured at 25°C, which may not be the same at the test temperature. A short period of time elapsed (less than 20 minutes) between removal of a fluid sample from the autocalve and filtration. The authors agree that colloidal and particulate material may be formed during this interval. Also, the solution samples were cooled to room temperature from 200°C which could also contribute to error in the analysis of the components. Equilibrium was not reached in these experiments. Therefore, the concentrations at the conclusion of the tests are not the solubility limit values at the test temperature.

3.2.3.1 Tabulation of Solubility Data for Neptunium

The neptunium solubility data reported are mostly for neptunium hydrous oxide or neptunium oxide, with a few data for neptunium doped glass. These are shown in Table 3.15. There is a wide variation in the reported data from 10^{-10} to 711 ppm depending on the conditions used in the experiments. From the Krauskopf data, the variation is relatively small (about 3 orders of magnitude) between the oxidizing and reducing conditions. However, between Salter's reducing condition data and Kerrisk's oxidizing-condition data, the variation is much larger (about 12 orders of magnitude).

Table 3.15 Solubility of neptunium

Reference	Solubility (ppm)	Conditions
Table compiled by Krauskopf (Ref. by Pigford, et al, 1983)	10^{-3}	Not specified
	10^{-4}	Reducing (Eh = -0.2V) pH = 6 and 9
	10^{-2}	Oxidizing (Eh = 0.2V) pH = 9
	10^{-1}	Oxidizing (Eh = 0.2V) pH = 6
Early (1983)	2.4×10^{-5}	Computed solubility in groundwater under reducing conditions.
	9.5	Sorption experiments.
Salter (1982)	2.4×10^{-10}	Basalt groundwater under reducing conditions. (Estimated from thermodynamic and laboratory data).
Ogard & Kerrisk (Ref. J. F. Kerrisk, LA-UR-84-3054, 1984)	711	Tuff groundwater (Yucca Mountain) under oxidizing conditions.
Krupka (1984)	1.8×10^{-3}	Carbonate free water containing 100 ppm F. ph ≈6
Strickert (1983)	0.024 to 2.4	Solution under a neutral atmosphere. pH = 4 to 12
Schramke (1984)	3×10^{-2}	Synthetic basaltic groundwater at 200°C (Basalt was present in the test. This may not be a solubility limit value).

3.2.4 Uranium

Among the various radionuclides, uranium has been the subject of the most extensive leaching and solubility studies reported in the literature. Most of the solubility studies have been conducted at 25°C. A few dissolution studies were conducted at higher temperatures.

The major isotope of uranium present in spent fuel or vitrified high-level waste is U-234, which has a half-life of 2.45 x 10^5 years. Although the radioactivity of uranium in the waste is less than one percent of the total activity after the containment period of 300 - 1000 years, the leaching or solubility of UO_2 can yield useful information that is applicable to other radionuclides. For this reason, a review of this information is given below. Also, the dissolution of UO_2 is of great significance with regard to the matrix dissolution of spent nuclear fuel.

Krupka and others (PNL-SA-12324, 1984) reported solubility data for U(VI) hydroxide. The MCC-3S "Agitated Power Leach Test" was used with modifications. The solubility measurements were made at 25°C in carbonate free water, under oxidizing to mildly reducing conditions in a pH range of 3 to 11. Saturation was approached from both an undersaturated and oversaturated condition. Experiments in which the solubility limit was approached from a condition of undersaturation involved the equilibration of $UO_3 \cdot 2H_2O$ (schoepite) with carbonate-free distilled water. Experiments that approach the solubility limit from oversaturation involved the adjustment of the pH of $HClO_4$ solutions containing 2750 ppm U(VI). The U(VI) solution was monitored every 7 days until "equilibrium" conditions were assured. The solutions were then filtered. Solution concentrations were determined by laser-induced fluorescence and the solid materials characterized by X-ray diffraction and scanning electron microscopy. Figure 3.10 is a reproduction of the data reported by Krupka and others, and Table 3.16 gives an estimate of the points reported in Figure 3.10.

U(VI) concentrations tend to be larger when equilibrium is approached from a condition of oversaturation, particularly in the region of near-neutral pH. The authors postulated that differences in crystallinity or composition of the controlling solids may have resulted in some of the observed differences, although they note that the agreement in the U(VI) concentrations in the acid and base pH range would tend to indicate that the same solid phase controls equilibrium in these regions. Schoepite was identified as the solid present in the undersaturated experiments, but no solid phase data conclusively indicated its presence in the oversaturated experiment.

The MINTEQ geochemical reaction code was used to calculate the solubility of $UO_3 \cdot 2H_2O$ using published thermodynamic data for schoepite and U(VI) hydroxyl complexes. The dashed line (Fig. 3.10) is the calculated solubility, using data which do not include any anionic hydroxyl complexes. Using data for an anion hydroxyl complex in conjunction with revised hydrolysis constants resulted in better agreement between the experimentally measured solubility and the calculated solubility (solid line in Fig. 3.10).

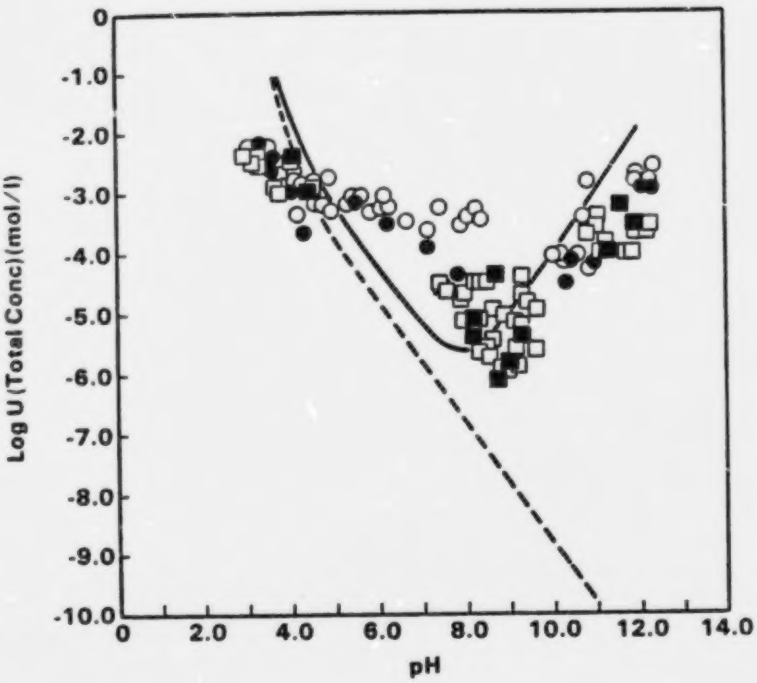

Figure 3.10 Measured concentrations of dissolved U in contact with U(VI) hydroxide at 25°C.

[The solubility data from the under- and over-saturated experiments are represented by square and circle symbols, respectively. The filled symbols represent the U concentrations measured at 14 and 9 days (the first sampling period), respectively, for the under- and over-saturated experiments. The open symbols represent U concentrations measured between 14 to 53 days of solution equilibration. The solubility calculated for schoepite ($UO_3 \cdot 2H_2O$) at 25°C under carbonate-free, oxidizing conditions using the thermodynamic data reported by Langmuir [8] is shown by the dashed line. The U(VI) hydroxyl complexes listed by Langmuir [8] include UO^{2+}, UO_2OH^+, $(UO_2)_2(OH)^{2+}$, and $(UO_2)_3(OH)+$. The solid line represents the solubility calculated for schoepite using the thermodynamic data for 1) the species UO^{2+}, $UO_2(OH)^+$, $(UO_2)_2(OH)^{2+}$, $(UO_2)_3(OH)^{2+}$, $(UO_2)_3(OH)^+$, and $(UO_2)_4(OH)^2$ from Sylva and Davidson [18]; 2) the species $UO_2(OH)^0(aq)$ and $(UO_2)_3(OH)_7$ from Lemire and Tremaine [9]; and 3) the $\Delta G^0{}_{,298}$ for schoepite from Langmuir [8].] Reproduced from PNL-SA-12324, 1984.

Table 3.16 Estimated maximum and minimum concentrations of U(VI) versus pH. Values are estimated from the graphical presentation (see Figure 3.10) and do not include an estimate of errors involved in estimating the value of the data points.

Maximum Concentration Log (M/L)	Condition	Minimum Concentration Log (M/L)	Condition	pH	Range (ppm)
-2	O[a](9-53d)	-2.5	U(14-53d)	3	700-2300
-2.4	U(9-53d)	-3.3	O(14-53d)	4	120-930
-3.3	O(14-53d)	-	-	5	-120
-3.0	O(14-53d)	-3.5	O(9-14d)	6	70-230
-3.5	O(14-53d)	-3.8	O(9-14d)	7	40-70
-4.3	O(9-14d)	-5.3	U(9-14d)	8	1-10
-4.3	U(14-53d)	-5.8	U(9-14d)	9	4-10
-4.0	O(14-53d)	-4.4	O(9-14d)	10	10-20
-2.7	O(14-53d)	-4.1	O(9-14d)	11	20-470

a: O is oversaturated, and U is undersaturated

U(VI) hydroxide has been identified as one of the solid phases which may limit the maximum concentration of U(VI) dissolved in oxidizing to mildly reducing groundwater. The solubility of U(VI) hydroxide has been used in a source term model for radionuclide release from spent fuel. The objectives of the work by Krupka and others are to extend the pH range over which the solubility has been determined and to assess the importance of anionic hydroxyl complexes of U(VI) in near neutral to alkaline conditions.

Several factors should be noted when evaluating the applicability of this work and the data to the conditions anticipated in a repository following the containment period. Krupka employed a standardized, reproducible procedure. "Equilibrium" or steady state was approached from both a condition of oversaturation and undersaturation. The starting material was characterized, the end product solid identified where possible, and concentrations were determined over a period of time. All of these steps are necessary for measuring solubilities; however, the usefulness of the data is limited by the "system" studied, and the conditions used. Distilled water, not repository water, was the medium. Only a single temperature, lower than most anticipated repository ambient temperatures, was used. Only dissolved U(VI) concentrations are reported. Other components of the repository system are not present (e.g., packing materials, host rock, container corrosion products, etc.), and no long term studies appear to have been done to insure that the steady state condition achieved after 53 days is in fact an equilibrium system. In general, the system studied bears little resemblance to the system anticipated in the repository.

The report also points to several difficulties in the determination of solubilities in even a relatively simple system. The first is that the end products in the oversaturated experiments could not be identified. The authors indicate that this may be due to the nature of the U(VI) solid, i.e., amorphous), or the mass of U(VI) solid present is small relative to the mass of $NaClO_4$ and it cannot be detected. In a more complex system (e.g., one containing host rock, packing material, etc.), one would anticipate that identification of all end run products may not be feasible or in many instances possible.

There is no guarantee that equilibrium has been achieved at all pH values. The concentrations reported for near neutral pH for tests in which equilibrium is approached from a condition of oversaturation are in some instances as much as 3 orders of magnitude larger than concentrations reported for the undersaturated experiments. Furthermore, without an indication of the precision in the measurement techniques, and whether each point for a given sampling time and pH are single data points or represent replicate samples, the differences in concentration determined in each experiment could fall within the inherent uncertainties or represent real differences in the data. Assuming that each point is a single data point and taking all the data presented, there is an order of magnitude uncertainty in the solubilities at low and high pH and a three order of magnitude uncertainty in the near neutral pH range.

The solubilities are calculated using current thermodynamic data and the assumption of anionic hydroxyl complexes and a fit to all the data presented. While the data and fit would indicate 2 to 3 orders of magnitude smaller solubility in the pH range anticipated for most repository water (pH 6-9), if one were to consider only the longer term oversaturated data and assume, at best, an order of magnitude uncertainty in each point, a conservative estimate of the solubility in the pH range of 4 to 11 would be 10^{-3}M (200 ppm).

Wilson et al, (1985), studied the solubility of radionuclides from PWR spent fuels in J-13 groundwater obtained from the Yucca Mountains site in Nevada. In the investigation, which is part of the Nevada Nuclear Waste Storage Investigation Project (NNWSI) Spent Fuel Leaching/Dissolution Test Program, radionuclide release is measured from spent fuel specimens representing a range of possible fuel degradation states thought to be possible during the post-containment period. Four test specimens were used:

- bare fuel plus split cladding hulls
- slit defect on the cladding
- hole defects, two laser-drilled holes in the cladding
- undefected rod sections

The tests were run in air at ambient hot cell temperature.

A test vessel containing the specimen was initially filled with 250 mL of J-13 water. Solution samples of 10-25 mL were periodically removed and replaced with fresh J-13 water. At the end of a test run, the final solution, the specimens, and water used to rinse deposits off the apparatus were all analyzed. These test results are compared with earlier tests carried out in deionized water.

Uranium content in unfiltered solution samples is plotted in Figure 3.11 for the various tests. Uranium concentrations in the J-13/Turkey Point (TP) bare fuel test remained nearly constant at 4 to 5 mg/mL. In the DIW/H.B. Robinson (HBR) bare fuel test, it decreased to 1.2 mg/mL from a maximum of 4.5 mg/mL. In the DIW/TP bare fuel test, the U content fluctuated to a greater extent. A 202-day solution sample had shown the presence of colloids or fine undissolved particles of uranium. When the test was continued to 250 days, it appeared that much of this colloidal phase may have precipitated.

Plutonium solution activities in the DIW/TP tests were in general about an order magnitude higher than those measured in the J-13 water tests.

Due to the high activity and solubility of Cs-137 in the fuel/cladding gap, Cs-137 solution activity provides a means to monitor test performance. The relatively fast buildup of Cs-137 solution activity in the slit defect and hole defects tests to levels approximately equal to those in the bare fuel tests indicated that the water entered and filled the fuel/cladding gap. The fact that no increase occurred in Cs-137 solution activity in the undefected specimen tests indicated that these fuel specimens did not leach.

Fractional release of each radionuclide was calculated by dividing the total measured release by 10^{-5} of the radionuclide inventory, and the results are shown in Table 3.17. Even though, the total release for each of the radionuclide was calculated for the duration of the test (223 days), in all the bare fuel tests, the total release was more than the NRC limit of 10^{-5} of the inventory per year.

Table 3.17 Total measured release divided by 10^{-5} inventory.

	Series[a]	Bare Fuel	Slit Defect	Hole Defects	Undefected
Uranium	J-13/HBR	5.42	0.044	≈0.005	<0.008
	DIW/TP	21.2	0.065	0.032	0.010
Pu-239+	J-13/HBR	7.04	0.008	≈0.002	≈0.002
Pu-240	DIW/TP	22.4	0.20	0.042	0.021
Am-241	J-13/HBR	7.76	0.008	≈0.002	≈0.003
	DIW/TP	17.2	0.152	0.019	0.008
Cm-244	J-13/HBR	6.54	0.007	0.001	≈0.002
	DIW/TP	21.5	0.35	0.026	0.006
Np-237	J-13/HBR	≈6.4	--	--	--
	DIW/TP	≈18	≈0.2	--	--
Cs-137	J-13/HBR	683	567	362	≈0.7
	DIW/TP	≈230	110	50	0.04
Tc-99	H-13/HBR	20.2	2.46	≈1	--
	DIW/TP	152	81	--	--

[a]: HBR: H.B. Robinson spent fuel.
TP: Turkey Point spent fuel.

The conclusions from the above table are:

1) greater release occurred in the DIW/TP tests relative to the J-13/HBR tests;

2) actinides appear to be released congruently based on similar fractional release values; and

3) Cs-137 and Tc-99 are released preferentially relative to the actinides.

Solution pH was measured in the various tests. A comparison of the change in pH is shown in Figure 3.12.

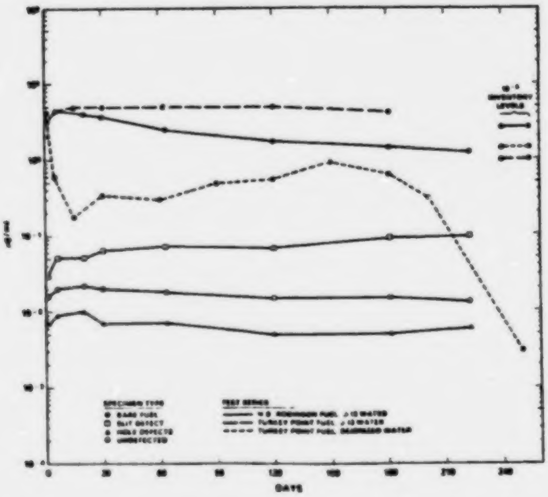

Figure 3.11 Uranium in unfiltered solution for different test specimens.

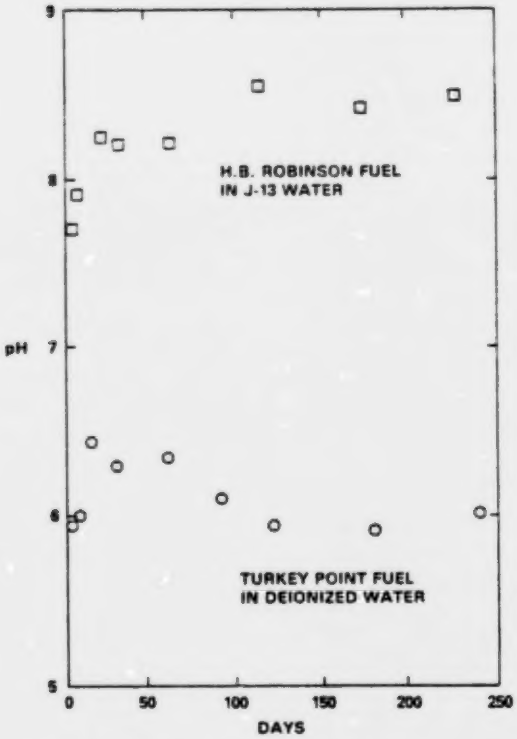

Figure 3.12 pH of solution samples taken from the H.B. Robinson fuel in J-13 water and Turkey Point fuel in deionized water - bare fuel tests.

The J-13 water, containing about 120 µg/mL bicarbonate, became slightly basic during the tests, while the deionized water became slightly acidic. The pH of the latter dropped to about 6 and remained around that value. Lower pH in the deionized water test may have resulted from radiolysis of dissolved air and water producing HNO_3. This HNO_3 radiolysis product would not have much effect on the J-13 water pH because of buffering by the bicarbonate.

The investigation gives an understanding of the radionuclide solubilities in tuff groundwaters and deionized water. It also shows the effects of various defects on the spent fuel rods on the solubility and radionuclide release rate. However, there is some concern about the semi-static conditions used in the tests. A sample of up to 25 ml is about 10 percent of total solution in the test vessel. When several such samples are taken and replenished with fresh solution, it could cause error in the final analysis of the leaching rate. If indeed a 25 ml sample was necessary, the test should have been carried out with a higher volume of test solution.

Nykyri (1985) studied the solubility of unirradiated fuel in granite groundwaters. Although granite groundwater is of limited interest for this study, the paper is reviewed to understand the effect of leachant variables on UO_2 dissolution.

The dissolution experiments of unirradiated uranium oxide pellets in this work were carried out in oxygen-free containers and a glove box, and in an anaerobic autoclave system. Two different synthetic groundwaters corresponding to undisturbed groundwaters deep in the granite bedrock, and another with high carbonate content, were employed in these tests. The high carbonate groundwater takes into account the effects of bentonite present around the spent fuel canisters in the repository. Two natural groundwaters were also used. Other experimental conditions were:

pH	4.5 to 11
Eh	0.1 to -0.4 V
Temperature	25°C and 60°C

The compositions of the groundwaters used in the experiments are shown in Table 3.18. The tests were carried at a pressure of 10 MPa. The pH is adjusted by varying the composition of $HCO_3^- - CO_3^{-2} - OH^- - H^+$. The Eh was controlled by Fe(II) content.

The dissolution rates of uranium in the various leaching solutions are shown in Table 3.19. The dissolution rate varied from 2×10^{-8} to 2×10^{-7} g cm^{-2} d^{-1} at pH 8 to 9. From the table, it is seen that there is a wider range for the dissolution rate values in the literature, i.e., 10^{-9} to 10^{-6} g cm^{-2} d^{-1}. The carbonate in the solution enhances the dissolution rate. The Eh has a great influence on the dissolution rate; i.e. less dissolution for lower Eh. Even with higher carbonate content, the dissolution stays low if a low Eh is maintained.

Table 3.18 Groundwater compositions.

Component		Dimension	Olkiluoto groundwater (Sample YD2, 70m, 30.8.1982) (natural)	Stripa groundwater (Sample M3/82-09/1) (natural)	Undisturbed granite groundwater[1] (synthetic I)	Groundwater in the presence of bentonite clay[8] (synthetic II)
pH		1	8.2	8.3	8...9	8...9
Eh		V	-	-	-0.1	-0.4...0
Alkalinity		mval/l	5.9	1.4	-	-
Electric conductivity		mS/m	8.7	28	-	-
Permanganate number	$KMnO_4$	mg/l	50	4	-	-
Phosphate	PO_4^{3-}	mg/l	.011	< 0.1	-	0.01
	HPO_4^{2-}	"	-	-	-	0.4
Sulphate	SO_4^{2-}	"	180	6.0	9.6	50
Chloride	Cl^-	"	20	37	70	80
Fluoride	F^-	"	0.47	5.3	-	7.5
Bicarbonate	HCO_3^-	"	360	86	120	400...600
Nitrite	NO_2^-	"	< 0.1	< 0.001	-	-
Nitrate	NO_3^-	"	< 0.1	< 0.02	-	-
Iron	Fe_{tot}	"	0.04	< 0.02	(2...3)	< 5
Silica	SiO_2	"	13 (Si)	< 1	12	20
Potassium	K^+	"	17	0.26	3.9	5
Sodium	Na^+	"	77	50	65	300...500
Ammonium	NH_4^+	"	< 0.01	< 0.01	-	-
Calcium	Ca^{2+}	"	69	14	18	20
Magnesium	Mg^{2+}	"	39	0.25	4.3	5
Manganese	Mn^{2+}	"	1.3	< 0.02	-	-

Table 3.19 Dissolution rates of uranium.

Water	Oxygen content (mg/l)	Temp. (°C)	Dissolution rate (g cm^{-2} d^{-1})	Time
Deionized	8...9 Air-saturated	25	$5 \cdot 10^{-8}$	After 732 d
Olkiluoto groundwater	< 0.01 Oxygen-free	25	$1 \cdot 10^{-7}$	After 612 d
Stripa groundwater	"	25	$2 \cdot 10^{-7}$	"
Olkiluoto groundwater	2...3 Mildly oxidizing	60	$2 \cdot 10^{-8}$	"
Stripa groundwater	"	60	$2 \cdot 10^{-7}$	"
Literature[6]	-	-	$10^{-9}...10^{-6}$	-

Figure 3.13 shows the effect of pH on uranium solubility in synthetic groundwaters. From preliminary tests, it is seen that for higher carbonate content groundwaters, the solubility increases as pH increases. However, at pH 8-9, the solubility value is lower than at pH 4-5. This needs to be confirmed. If indeed, the solubility decreases, it is possible that some other mechanism may be involved, such as precipitation of uranium from the solution.

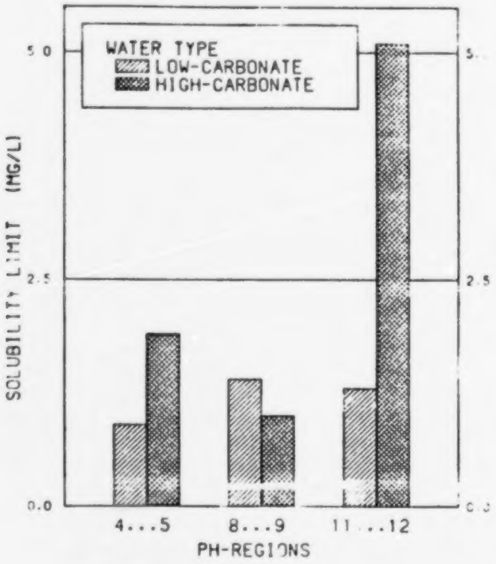

Figure 3.13 Solubility limit of uranium as a function of pH. (The low-carbonate water refers to synthetic groundwater I and the high-carbonate water to synthetic groundwater II.) (Ref. Nykyri (1985))

The investigations confirm that the solubility of uranium in granite groundwater varies strongly with the groundwater conditions. As a preliminary investigation, the results are useful in developing the test methods and to check the effect of pH, Eh and chemical composition of the groundwater on the solubility of uranium.

Peters and Diamond (PNL-3971, 1981) studied the effect of dissolved oxygen on the leaching of plutonium, neptunium and uranium from a simulated borosilicate glass (PNL 76-68). These tests were conducted at temperatures of 25°C and 75°C and in deionized water, 0.03 M NaHO$_3$ and WIPP "B" salt brine for periods up to 341 days. For uranium, the total dissolution in salt brine and deionized water at 25°C was decreased by factors of 2 to 5 in deaerated solutions. However, at 75°C there was no significant effect due to deaeration on uranium leaching.

The redox conditions were not monitored in the above investigation. Radiolysis due to alpha activity of Np-237 and Pu-239 may generate oxidants in the leachate, which can increase the solubility. Therefore, to fully understand the effect of aeration and deaeration conditions, the leachates should be redox-buffered.

A dissolution study for uranium-doped DWRG was reviewed earlier in the section 3.2.2 for the release rate of plutonium. This is part of the PNL report, "Final Report of the Defense High-Level Waste Leaching Mechanisms Program," (PNL-5157, August 1984). In the dissolution study using brine and reference basalt groundwater, the uranium concentrations were also measured. The leaching tests were conducted with or without an iron coupon present in the solution.

Test data for one of the solutions, viz., basaltic waste, are shown in Figures 3.14 and 3.15. Table 3.20 summarizes the total release of uranium in each solution and the relative percentage of that associated with colloids, true solution (filtered), the iron coupon, and the acid strip of the vessel walls. The latter two give uranium concentrations absorbed on the iron coupon and vessel walls.

In the basaltic water, when the iron coupon is absent, essentially all of the uranium released is soluble with negligible amounts of filterable colloidal uranium or uranium sorbed onto the container walls. The results of this test are similar to the brine solution test results, but the total amount of uranium released after 56 days is higher by a factor of 10 for the basaltic groundwater. Within analytical uncertainties, the data for uranium release from a Pu-doped glass are identical to the data for uranium release from a Np-doped glass for the basaltic groundwater tests. Uranium also shows a qualitatively similar behavior for release from both glasses when tested in basaltic groundwater plus iron. The amount of filterable colloidal uranium is greatly increased by the presence of iron.

It is seen from Table 3.20 that for 56-day duration the total uranium released from the test sample increased in the presence of iron by a factor of 4 in brine and by a factor of 2.5 in basaltic water.

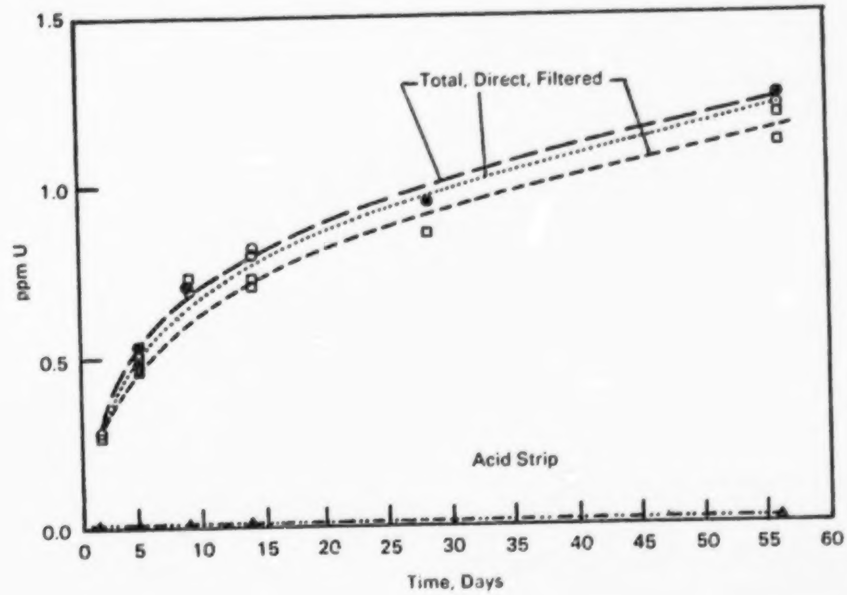

Figure 3.14 Uranium release from Np-doped glass in basalt solution (90°C).

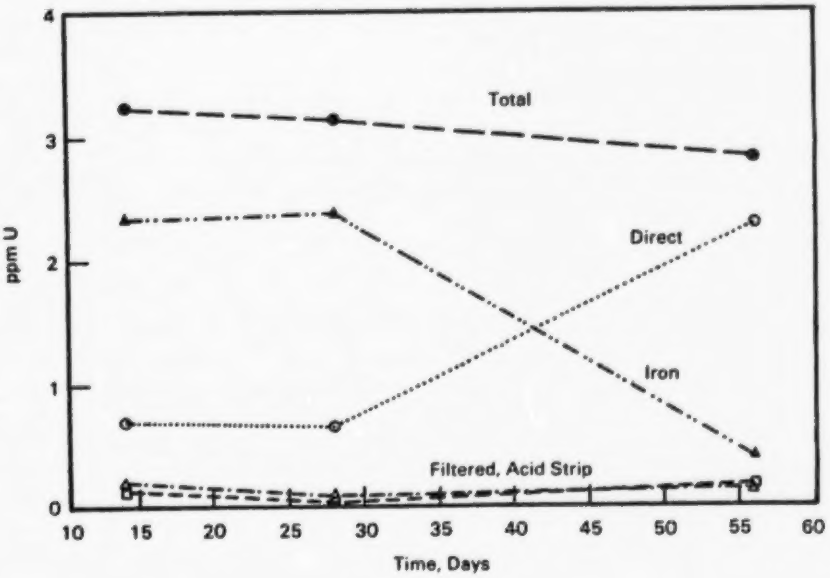

Figure 3.15 Uranium release from Np-doped glass in basalt solution with iron (90°C).

In all the experiments, the total amount of uranium released was still increasing, even at the end of the 56-day period, except for basaltic water with iron present, in which case it was decreasing. Therefore, the solubility limit or steady state conditions have not been achieved in all the experiments.

Table 3.20 Systems of uranium release after 56-day duration[(a)].

System	Total Release (ppb)	Colloidal	Filtered	Iron	Acid Strip
Brine	0.56 ± 0.10	<1%	5%	-	95%
Brine + Iron	2.17 ± 0.12	80%	<1%	10%	10%
Basalt + Water	1.10 ± 0.15	<1%	100%	-	<1%
Basalt + Water + Iron	2.86 ± 0.15	75%	5%	15%	5%

(a) Leach tests at 90°C.

The above investigations have some limitations, since several other repository conditions have not been incorporated in these experiments. First, some waste package components such as the packing are not included in the experiments. The experiments should also have been conducted for a longer duration until the solubility limits were reached.

Ogard and Duffy (1981) measured the solubility of UO_2 in 25°C deionized water, at pH ≈ 4 under reducing conditions. Equilibrium was approached from a condition of undersaturation only. They compared their data to those estimated from data by Langmuir (1978) for U in solution and in equilibrium with crystalline and amorphous UO_2. Figure 3.16 is a reproduction of the estimated solubilities. Figure 3.17 shows the measured solubilities at pH=4 over a period of 120 days, and Table 3.21 gives estimates of the values reported in Figure 3.17. In Figure 3.16, the numbers shown on each curve represent oxygen fugacities. For example, -80 indicates that the oxygen fugacity is 10^{-80} atmospheres.

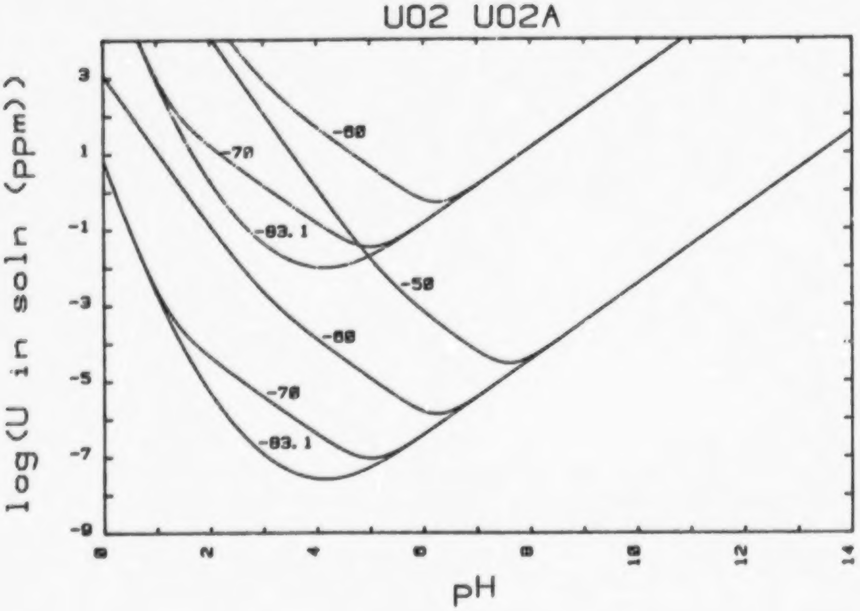

Figure 3.16 Solubility of UO_2 in water as a function of pH and $f(O_2)$. (Ogard and Duffy, 1981).

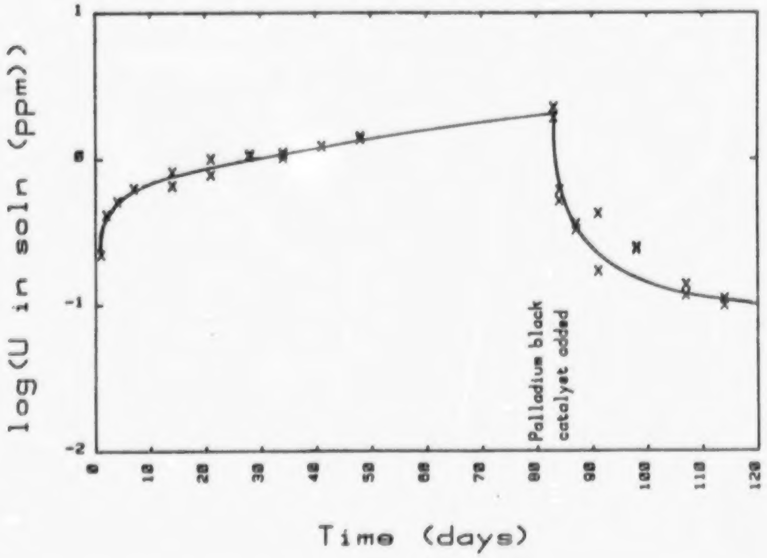

Figure 3.17 Time dependence of uranium concentration. (Ogard and Duffy, 1981).

Table 3.21 Estimated solubilities for UO_2 at pH=4 in DIW, 25°C. (Data from Figure 3.17).

Approximate Time (days)	Log [U conc. (ppm)][a]	U Concentration (ppm)
1	-0.5	0.3
5	-0.25	0.6
27	0	1
84	>0.25	2
84[b]	-0.25	0.6
90	-0.5	0.3
100	-0.75	0.2
120	-1	0.1

a) Predicted solubility at pH=4 varies from $\approx 10^{-7}$ to 10^{2} ppm for O_2 fugacities between 10^{-83} and 10^{-60} atmos. and $UO_2(c)$ vs $UO_2(a)$.

b) Palladium black added after 84 days

Even after the addition of Pd black catalyst, the measured concentration of U in solution shows a maximum uncertainty of 6 orders of magnitude with respect to the calculated values. This uncertainty depends on the final fugacity of O_2, the species in solution, and the solid form controlling the solubility. However, such information is not given in the paper. It is assumed that the method used for establishing reducing conditions (i.e., purging with H_2) is inadequate for ensuring low O_2 fugacities even though the measured Eh is low (-180 to -220 mV).

Ogard and Duffy also measured the solubility of H. B. Robinson spent fuel elements in DIW. They used an IAEA leach test and controlled the atmosphere above and in the solution to vary the Eh from oxidizing to mildly reducing. Two test temperatures, 25°C and 70°C, were used. The measured solubilities for selected radionuclides are given in Table 3.22.

Ogard and Duffy report average values (oxidizing and reducing conditions) for the solubilities at 25°C and 70°C for all elements except U at 70°C. They indicated that under oxidizing and reducing conditions the solubilities for Eu, Ce, Pm and Pu did not vary by more than a factor of 10. They also note an "apparent" negative temperature coefficient for these species. However, given the possible order of magnitude variation for the solubilities under reducing

Table 3.22 Radionuclide solubilities at pH=4, DIW. (Data from Ogard and Duffy).

Element	Concentration at 25°C[(a)]		Concentration at 70°C	
	(M)	(ppm)	(M)	(ppm)
Eu	≥3E-8		2E-9	
Ce	≥3E-7		1E-8	
Am	≥5E-8	0.012	2E-9	5E-4
Pu	3E-7	0.07	1E-8	2E-3
U[(b)]	>5E-5	12	>3E-4[(b)] ≈2E-6	70[(b)]

a) The concentrations are averages under both oxidizing and mildly reducing conditions.

b) Large value is for oxidizing conditions. The smaller value is for reducing conditions.

and oxidizing conditions, it is not clear that the differences determined as a function of temperature are meaningful. Furthermore, a comparison of the values obtained for the concentration of U in the presence of powdered UO_2, under reducing conditions at pH=4 and 25°C, with the "average values" reported for spent fuel leaching, show a factor of 10 to 100 variation depending on the value (time) selected for the comparison.

In general, this study illustrates two points. Figure 3.16 shows that after 84 days the concentration of U in solution is still increasing and steady-state had not been achieved. Therefore, the values reported for the leaching of spent fuel may not represent equilibrium concentrations. Without assurance that equilibrium has been achieved, these values only tend to add to the already uncertain data in the literature on solubility. The second point is that, as the authors point out, reducing conditions in which the O_2 content of the medium is at or near the fugacities predicted by thermodynamics are at best difficult to achieve and probably impossible. While purging with H_2 results in a negative Eh (drops from -180 to 220 mV) and the addition of palladium black catalyst appears to decrease the concentration of U in solution, this decrease may not be due to an increased reaction of H_2 purging gas with residual oxygen, but with the availability of a surface for sorption of U. It should also be noted that while reducing and oxidizing conditions are assumed, no data are presented to show the oxidation states in solution. While the reported solubilities are lower than those anticipated for U(VI) in equilibrium with schoepite, no information is provided to assure that the solubilities determined represent equilibrium or even steady state concentrations under defined conditions. For the values reported to be useful, it should be demonstrated that they are equivalent to or conservative with respect to concentrations anticipated in a repository following the containment period.

3.2.4.1 Tabulation of Solubility Data for Uranium

Uranium solubility values are for pure UO_2 or spent fuel. They are compiled in Table 3.23. Most of the values are for 25°C, except for the last reference in the table where values at 70°C are reported. Depending on the experimental conditions and the material used, there is a wide variation in results under oxidizing conditions. However, under reducing conditions, a value of 10^{-3}ppm seems to be a good conservative estimate for uranium solubility.

Table 3.23 Solubility of Uranium

Reference	Solubility (ppm)	Conditions
Table compiled by Kranskopf (Ref. by Pigford et al. 1983)	10^{-3}	Not specified
	10^{-3}	Reducing; pH = 9 (Eh = -0.2V)
	10^{-5}	Reducing; pH = 6 (Eh = -0.2V)
Early (1983)	4.8×10^{-5}	Groundwater under reducing conditions (Eh = -0.3V)
Salter (1982)	2.4×10^{-3}	Basalt groundwater under reducing conditions
Ogard and Kerrisk (Ref. J. F. Kerrisk, LA-UR-84-3054, 1984)	880	Tuff groundwater (Yucca Mountain) under oxidizing conditions
Krupka (1984)	200	Carbonate free water under oxidizing to mildly reducing conditions. (A conservative estimate in the pH range 4 to 11).
Nykyri (1985)	1 to 2	Low carbonate content granite groundwater under anaerobic conditions (pH 4 to 11).
	1 to 2	High carbonate content granite groundwater under anaerobic conditions (pH 4 to 9).
	5	High carbonate content granite groundwater under anaerobic conditions, (pH 11
Ogard and Duffy (1981)	12	Spent fuel in DIW under oxidizing conditions (pH 4)
	70	Same as above but at 70°C
	0.5	At 70°C and reducing conditions

3.2.5 Technetium

High-level waste contains significant amount of technetium, a non-actinide isotope which due to its long half life (2.12×10^5 years) contributes significantly to the radioactivity after the containment period. A number of studies have been conducted for technetium release rates and solubility. The range of conditions at which these studies have been conducted vary a great deal with a temperature range of 22-90°C, pH range of 1 to 11 and in groundwaters as well as deionized water. The Eh values in most of the experiments were not controlled or monitored.

Khalil and White studied the solubility of technetium-doped MCC reference glass in dilute acid (pH=3.19) in static leach experiments at 50°C and 90°C. Figure 3.18 shows the cumulative concentration of technetium dissolved in the solution. The technetium release appears to be linear at both temperatures. They give an equation for the normalized fractional release for technetium as shown below:

$$\text{Normalized Fractional Tc Release} = \frac{dc}{dt} \cdot \frac{V}{A} \cdot \frac{10^{-3}}{F_{Tc}\ W_g}$$

where c is the concentration in mg/L, V is the solution volume (0.1 L), A is the surface area (0.8 cm^2 at 50°C and 1.06 cm^2 at 90°C), F_{Tc} is fraction of technetium in the glass (0.002 for the technetium-doped MCC reference glass), and W_g is weight of glass sample (0.200 gm for 50°C and 0.151 gm for 90°C). The release rate obtained from this glass dissolution experiment is strangely

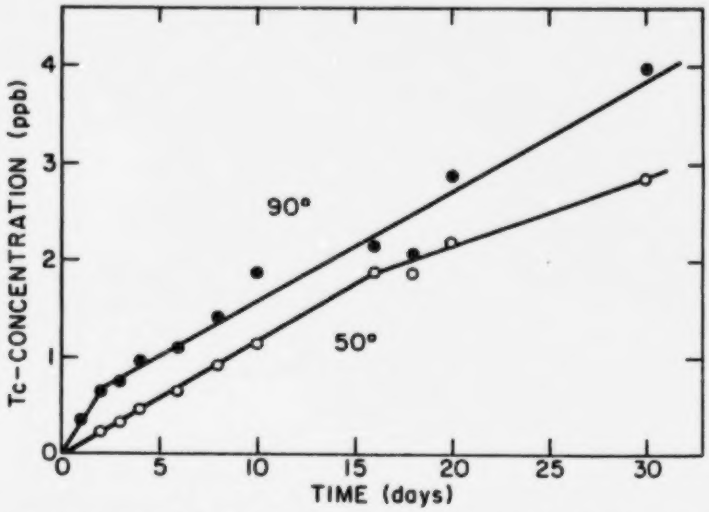

Figure 3.18 Dissolution of technetium-doped MCC reference glass in dilute acid at two temperatures. Data represent cumulative concentration as a function of time.

independent of temperature. The fractional release rate is 3.69 x 10^{-5} cm^{-2} day^{-1} at 50°C and 3.52 x 10^{-5} cm^{-2} day^{-1} at 90°C, identical within the limits of error.

A dissolution study was also conducted for technetium-doped MCC reference glass and magnesium titanate spinel ceramic in deionized water at 90°C. The cumulative fractions released are shown in Figure 3.19

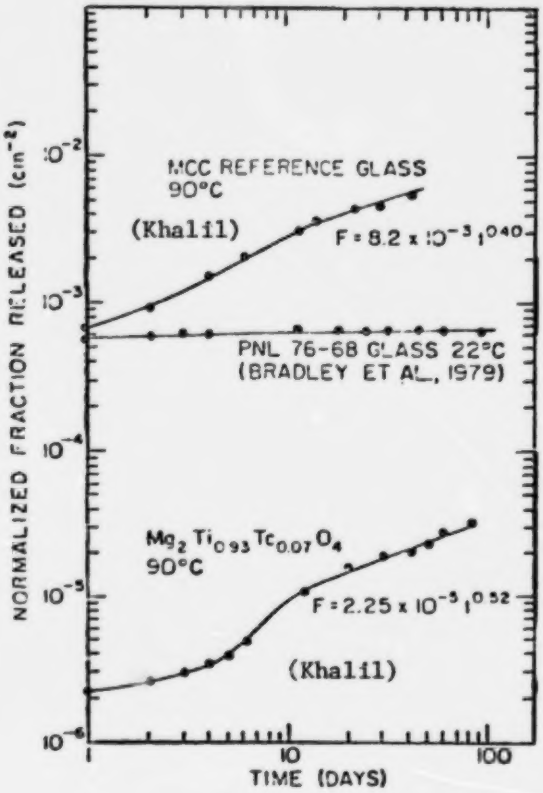

Figure 3.19 Cumulative technetium release as a function of time. All experiments in deionized water. Steady state pH ≈8.5 for both ceramic and glass. Glass SA = 14.4 cm^2 and spinel SA = 231 cm^2. (Khalil and White, 1984)

Bradley, et al. (PNL-3152, 1979) studied the dissolution of 76-68 glass containing Tc-99 in deionized water at 22°C. To compare their values with Khalil and White's, Bradley's data points were recalculated, as shown in Table 3.24 and both sets are given in Figure 3.19. After the initial fast release of technetium into the solution, there was not much further release for PNL glass, while it increased for MCC reference glass and ceramic spinel.

Table 3.24 Release of Tc-99 in deionized water
(Calculated from PNL-3152, p. A-11).

Cumulative Days	Cumulative Fraction Released	Concentration mg/L	Cumulative Normalized Fraction Released cm^{-2}
1	1.69×10^{-2}	1.86	5.58×10^{-4}
2	1.78×10^{-2}	1.96	5.88×10^{-4}
3	1.82×10^{-2}	2.00	5.88×10^{-4}
4	1.84×10^{-2}	2.02	6.07×10^{-4}
11	1.94×10^{-2}	2.13	6.4×10^{-4}
18	1.95×10^{-2}	2.14	6.44×10^{-4}
25	1.99×10^{-2}	2.19	6.56×10^{-4}
32	2.00×10^{-2}	2.20	6.6×10^{-4}
46	2.00×10^{-2}	2.20	6.6×10^{-4}
60	2.01×10^{-2}	2.21	6.63×10^{-4}
92	2.01×10^{-2}	2.21	6.63×10^{-4}

Bradley, et al. also carried out dissolution studies in WIPP Brine B and bicarbonate groundwater and the results are shown in Figure 3.20 along with the dissolution data for deionized water. There is little difference, and the cumulative fractions leached tend to a constant value in all three cases. The silicon leach rate, also plotted in Figure 3.20, shows a steady increase.

None of the above studies continued the experiments to the point where the technetium reached saturation level in solution. In the study by Khalil and White, the test time was less than 100 days, and the cumulative technetium release was still increasing. In the PNL study, the dissolution of technetium was limited by a small solid surface area for reaction with the solution. If, however, the test was continued further, there could have been additional technetium release as more silica dissolved. Note that the study was conducted at 22°C, while the repository would have a higher temperature after the containment period. The pH and Eh were not monitored in these investigations, and analysis of the glasses after leaching was apparently not reported.

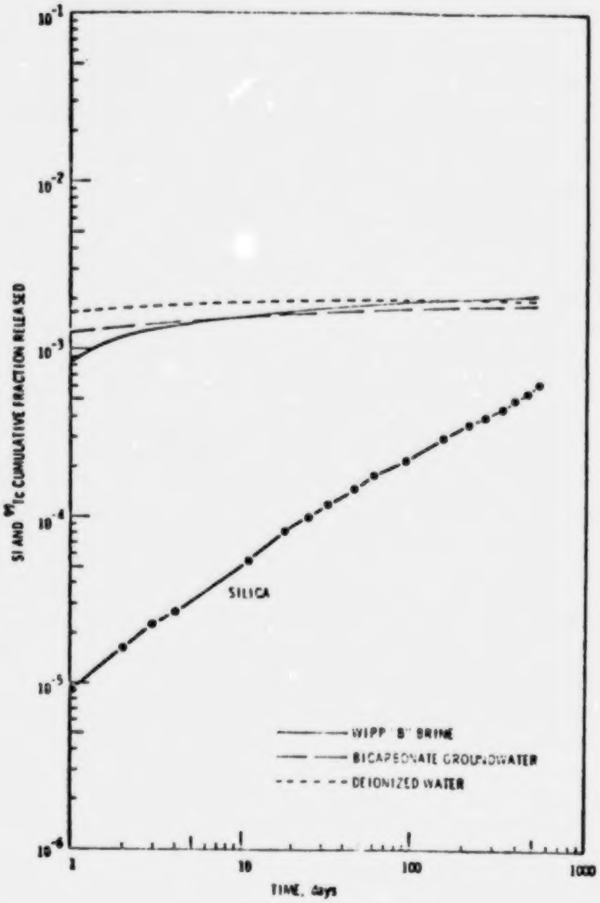

Figure 3.20 Cumulative fractions of Tc-99 released from simulated waste glass 76-68, IAEA leach test at 22°C.

Coles and Apted (1984) studied the hydrothermal interaction effect of glass/basalt on Tc-99 release from a borosilicate glass waste form. Crushed PNL 76-68 glass, doped with 0.7 mg Tc-99/g glass, was reacted with reference basalt groundwater under oxic hydrothermal conditions in a sampling autoclave, both alone and in the presence of crushed basalt. The steady state fluid concentrations of Tc-99 and various stable species were determined from samples obtained at the test conditions of 200°C, 30 MPa, and an initial solution to solid mass ratio of 10 for both tests. Nine solution samples were taken periodically at run conditions (200°C, 30 MPa). Each sample was split into three and two of them were filtered through 4,000Å and 18Å filters. A comparison of the analysis for these three samples provided a measure of the particle size association of Tc-99. It was assumed that material passing the 4,000Å filter was associated with either collodial particles, or was in true solution, and material passing the 18Å filter was in true solution.

Plots of the Tc-99 fluid concentration data for the two hydrothermal tests are shown in Figure 3.21. The Tc-99 fluid concentration for the unfiltered and the filtered solutions are also shown in the same figure. The residual solid phases were analyzed, but have not been reported yet in the literature.

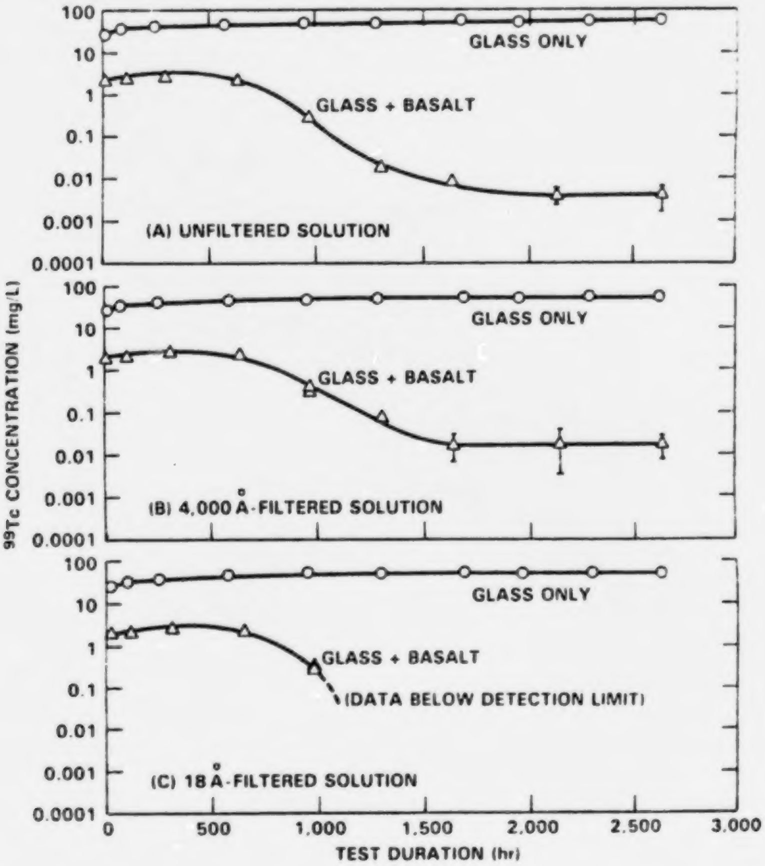

Figure 3.21 Technetium-99 concentrations versus test duration for solutions from 200°C/30 MPa tests on Tc-99 doped borosilicate glass.

In the glass + groundwater test, the Tc-99 concentration rose rapidly to about 50 mg/L after only 200 hr of run time and remained at a value between 50 and 60 mg/L throughout the duration of the test. For the basalt + glass + groundwater test, the Tc-99 concentration rose to an initial value of about 2.5 mg/L. At about 700 hr, the Tc-99 concentration began to drop rapidly until a value near the analytical detection limit (approximately 0.005 mg/L) was reached after a test duration of 1,400 hr. The presence of basalt in these hydrothermal experiments reduces the concentration of Tc-99 in solution by nearly four orders of magnitude, probably by control of solution Eh and subsequent precipitation of a solid containing a reduced form of technetium. When basalt is present in the system, the soluble TcO_4 is apparently reduced and removed from solution in some insoluble phase as can be seen from Figure 3.21A.

Figures 3.21B and 3.21C suggest that, technetium is present as a colloidal phase after 1,000 hours of reaction time, and the solution after fltration through a 18Å filter has undetectable amounts of Tc. This investigation shows the importance of conducting experiments at conditions similar to those in a repository. Over a long period of time, the presence of basalt has decreased the technetium solubility. However, as the authors point out, the test in this case has several limitations. First, other waste package components, such as the packing and metallic container materials are not included. These components may interact with the waste form causing unexpected or deleterious effects. Second, the groundwater used in these tests represents the undisturbed composition at a repository horizon. The composition of the groundwater that eventually will contact the waste form may be considerably altered from this composition. This alteration arises primarily from the sequential hydrothermal reactions between groundwater and waste-package components and also from the effects of potential gamma or alpha radiolysis. Thus, the groundwater composition may evolve during the progressive penetration of waste-package barriers before initial contact with the waste form. Third, the SA/V ratios used were approximations only and were used to promote steady state solution concentrations. Also, the hydrothermal conditions (200°C and 30 MPa) were selected assuming that a premature breach occurs for the waste package. However, after the containment period, the expected temperature is much higher as shown in Tables 1.2 to 1.4. To develop a good data base for technetium release, all these above factors need to be considered.

At PNL, dissolution of technetium containing crushed defense waste reference glass (DWRG) was carried out in solutions at different pH levels. (PNL-5157, 1984). The technetium content was 0.2 wt% of the glass. In all experiments, solid was added to 50 mL of solution. The starting pH level was adjusted by adding HCl or NH_4OH.

At sampling time, 1 mL of solution was taken for analysis, acidified with 1 drop of concentrated HCl, stored, and then analyzed by DC plasma atomic emission spectroscopy for all elements except technetium. An additional 0.25 mL of solution was added directly to the scintillation fluid and radioassayed for technetium.

Figures 3.22, 3.23 and 3.24 show the concentration of technetium as a function of time for temperatures 40, 70 and 90°C and at three pH levels; 1, 3 and 11.

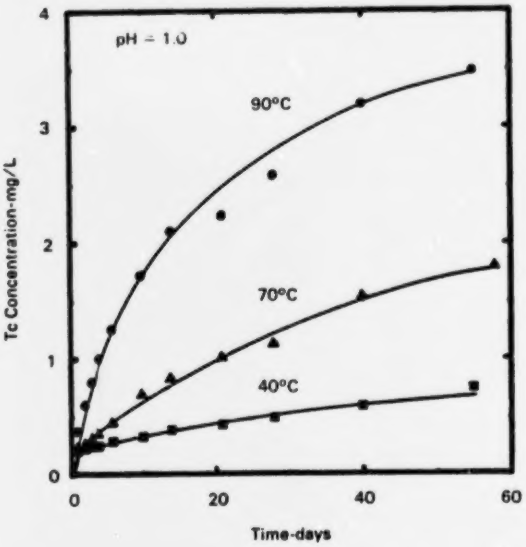

Figure 3.22 Technetium concentration versus time plot for the dissolution of DWRG glass in pH 1.0 solutions at 40, 70 and 90°C.

The effects of temperature can be clearly seen in Figure 3.22, the higher the temperature. the faster the dissolution of technetium. However, in pH 3.0 solutions (Figure 3.23), the dissolution rate is higher at 70°C than at 90°C. The authors attribute this to be the resullt of a high initial fast release of Tc at 70°C. Although at pH 11.0, there was a similar fast release at 70°C, the dissolution at 90°C was high enough to eliminate the effect of the initial fast release at 70°C at the same pH.

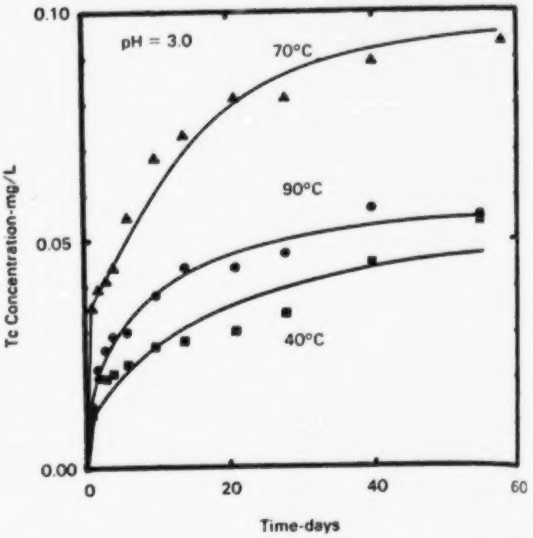

Figure 3.23 Technetium concentration versus time plots for the dissolution of DWRG glass in pH 3.0 solutions at 40, 70 and 90°C.

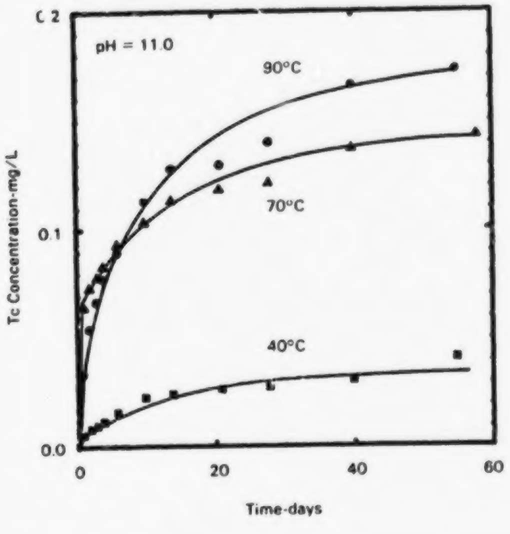

Figure 3.24 Technetium concentration versus time plots for the dissolution of DWRG in pH 11.0 solutions at 40, 70 and 90°C.

In order to compare the results of various studies, cumulative normalized fractional release (CNFR) values were calculated in each case. The equation given by Khalil and White, described earlier, was used. Since the actual data points were not tabulated in the PNL study, concentrations were obtained from the concentration versus time plots. The method of calculation and the cumulative normalized fractional release data are shown in Tables 3.25, 3.26, 3.27 and 3.28. In these calculations, the effects of SA/V, fraction of technetium in the glass and weight of glass sample on the release of technetium are normalized. Therefore, these results can be compared with the work done by Khalil and White, and Bradley, et al. All these results are plotted as shown in Figures 3.25 and 3.28.

Figure 3.25 shows the effect of pH on the cumulative normalized fraction of Tc released at 90°C. The shapes of the curves are similar in all cases, with an initial release of technetium followed by a gradual decrease in dissolution rate. Although for DWRG (PNL-5157), the initial fast release is higher for the experiment conducted at pH 11.00 than the one conducted in the deionized water (pH=5.6), the two curves cross after 16 days. It is interesting to note that for the experiment in deionized water, the pH increases to 8.5 at the end of the test while for the solution with initial pH 11.00, it decreases to 9.6. The results of Khalil and White for the dissolution of their MCC reference glass are 50 percent higher than for DWRG (PNL-5157), both being conducted in deionized water and both having a final pH of 8.5. This comparison shows the variation in the Tc release rates and concentration for different glasses.

Table 3.25 Calculation of cumulative normalized fraction released. (Data from PNL-5157).

$$\text{Cumulative Normalized Fraction Released (CNFR)} = C \cdot \frac{V}{A} \cdot \frac{10^{-3}}{F_{Tc} \cdot W_g}$$

C - Conc. mg/L
V - Solution vol. (L)
A - Surface area, cm^2

$$\frac{A}{V} = 0.29\ cm^{-1} \text{ for pH 1, 3 \& 11 and}$$

$$\frac{A}{V} = 0.47\ cm^{-1} \text{ for pH 5.6}$$

F_{Tc} - Fraction of technetium in the glass = 2×10^{-3}
Wg - Wt. of glass sample = 0.1 for pH 1,3 & 11
(gms) = 0.05 for pH 5.6

Table 3.26 Cumulative normalized fraction released for Tc at 90°C. (From PNL-5157).

Days	pH = 1		pH = 3		pH = 11	
	Conc. mg/L	CNFR x 10^{-3} cm^{-2}	Conc. mg/L	CNFR x 10^{-3} cm^{-2}	Conc. mg/L	CNFR x 10^{-3} cm^{-2}
1	0.4	6.8	0.014	0.24	0.037	0.64
5	1.2	20.07	0.03	0.52	0.081	1.4
10	1.75	30.2	0.038	0.66	0.112	1.93
15	2.20	38.00	0.044	0.76	0.13	2.24
20	2.45	42.2	0.047	0.81	0.142	2.45
30	2.85	49.1	0.051	0.88	0.157	2.70
40	3.20	55.0	0.054	0.93	0.166	2.86
50	3.40	58.6	0.055	0.95	0.17	2.93

Table 3.27 Cumulative normalized fraction released for Tc-99 in deionized water at 90°C. (PNL-5157).

	Starting pH 5.6	
Days	Conc. mg/L	CNFR x 10^{-3} cm^{-2}
1	0.02	0.426
4	0.04	0.85
9	0.08	1.7
16	0.11	2.34
25	0.135	2.87
36	0.158	3.36

Table 3.28 Cumulative normalized fraction released for Tc-99 at 40°C and starting pH 11.00.

Days	Conc. mg/L	CNFR x 10^{-3} cm^{-2}
1	0.005	0.0862
5	0.013	0.224
10	0.02	0.345
15	0.025	0.431
20	0.03	0.52
30	0.33	0.57
40	0.035	0.60
50	0.036	0.62

Table 3.29 Effect of final pH on cumulative normalized fractional release of Tc at 90°C. (Test duration: 56 days).

pH	CNFR, cm^{-2}
1	5.86×10^{-2}
3	9.5×10^{-4}
8.5	3.4×10^{-3}
8.5	6.0×10^{-3}
9.6	2.93×10^{-3}

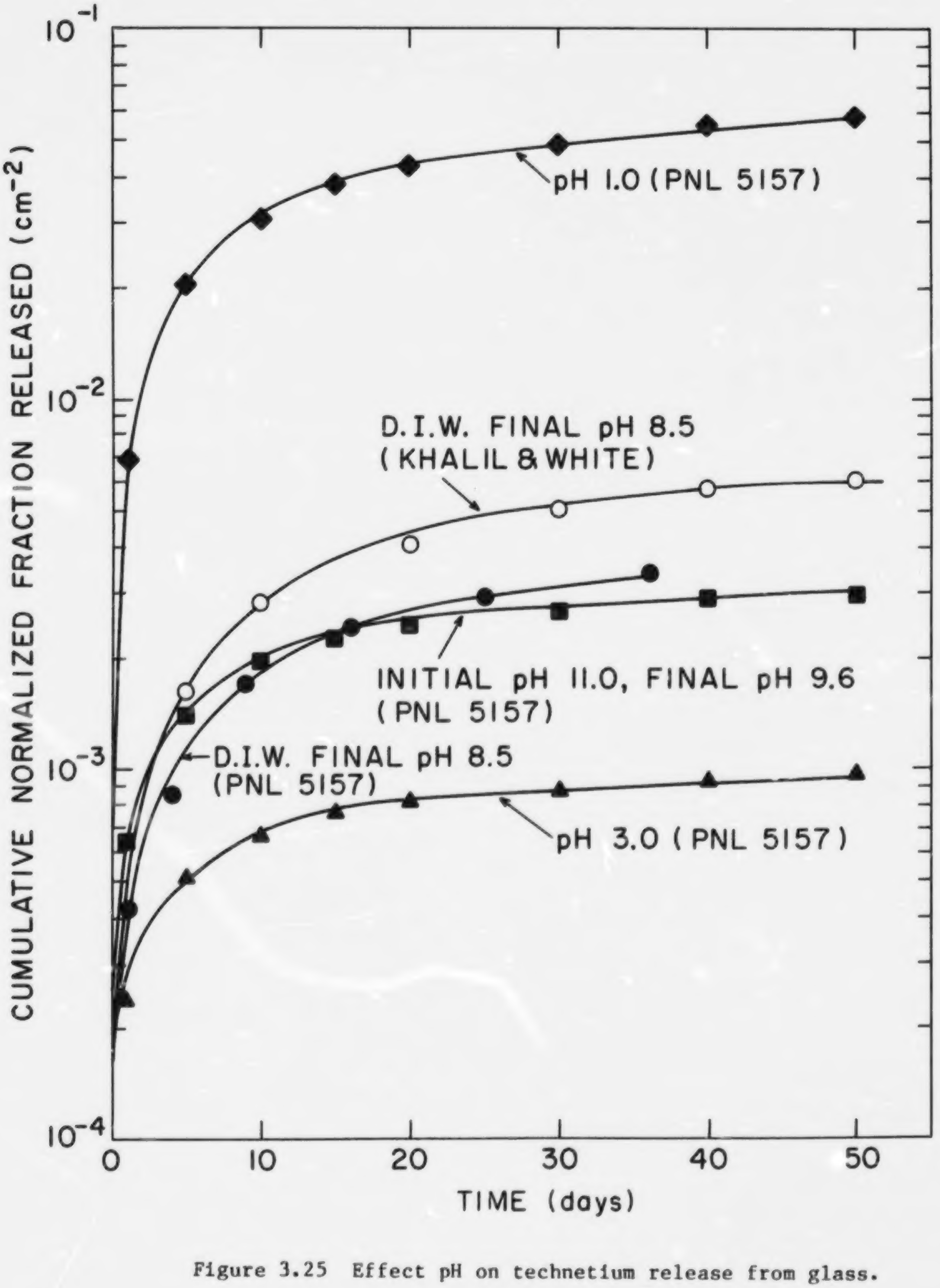

Figure 3.25 Effect pH on technetium release from glass.

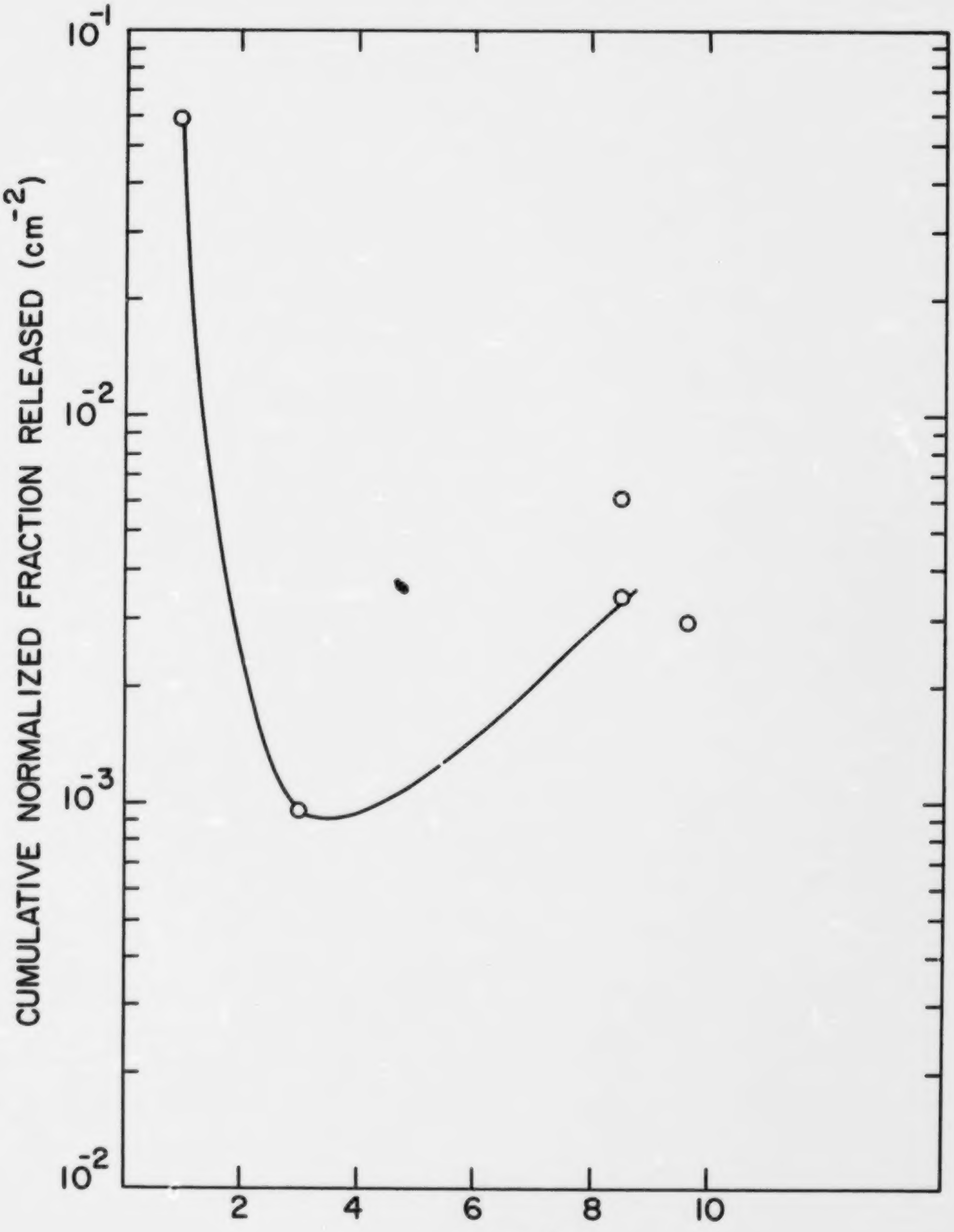

Figure 3.26 Cumulative normalized fraction released (cm^{-2}) versus final solution pH in Tc release experiments.

We can compare the shape of this curve to the leaching of SRP waste glass by Wicks (1982a) as shown in Figure 3.27. It seems that for technetium it tends to reach a minimum at around pH 3.0, although it cannot be confirmed whether it extends to neutral pH since there are no data in this range. For SRP glass, the minimum is in the neutral pH range. The pH value of 3.0 is still in the acidic range where the glass readily dissolves, therefore, it is interesting to see such a low solubility at this pH.

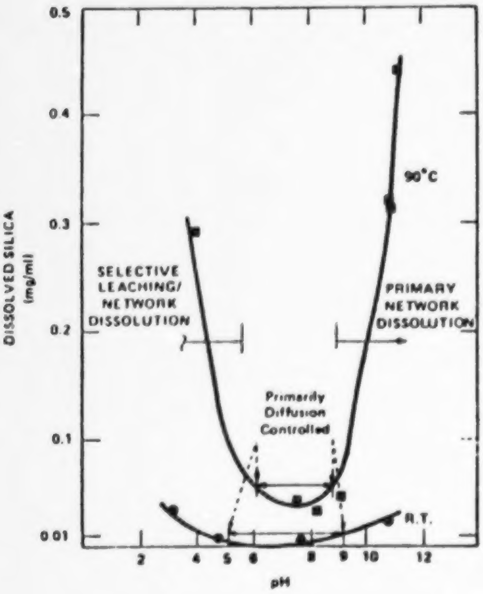

Figure 3.27 Effect of pH on leaching of SRP waste glass at temperatures (Wicks, G.G., 1982a)

To make a comparison of the Tc-99 release rate at lower temperature, Bradley's data on PNL 76-68 simulated borosilicate glass at 22°C were plotted along with the data on DWRG at 40°C and pH 10.0 (PNL-5157) and is shown in Fig. 3.28. Even with the neutral pH and lower temperature, the initial normalized release for technetium was seven times greater in Bradley's work compared to the data given in PNL-5157. One might expect a higher Tc-99 release at pH 11.0 and 40°C compared to neutral pH and 22°C. The dissolution rates are also different in both the cases. Therefore, these data do not help in making reliable predictions of temperature or pH dependence of Tc-99 release.

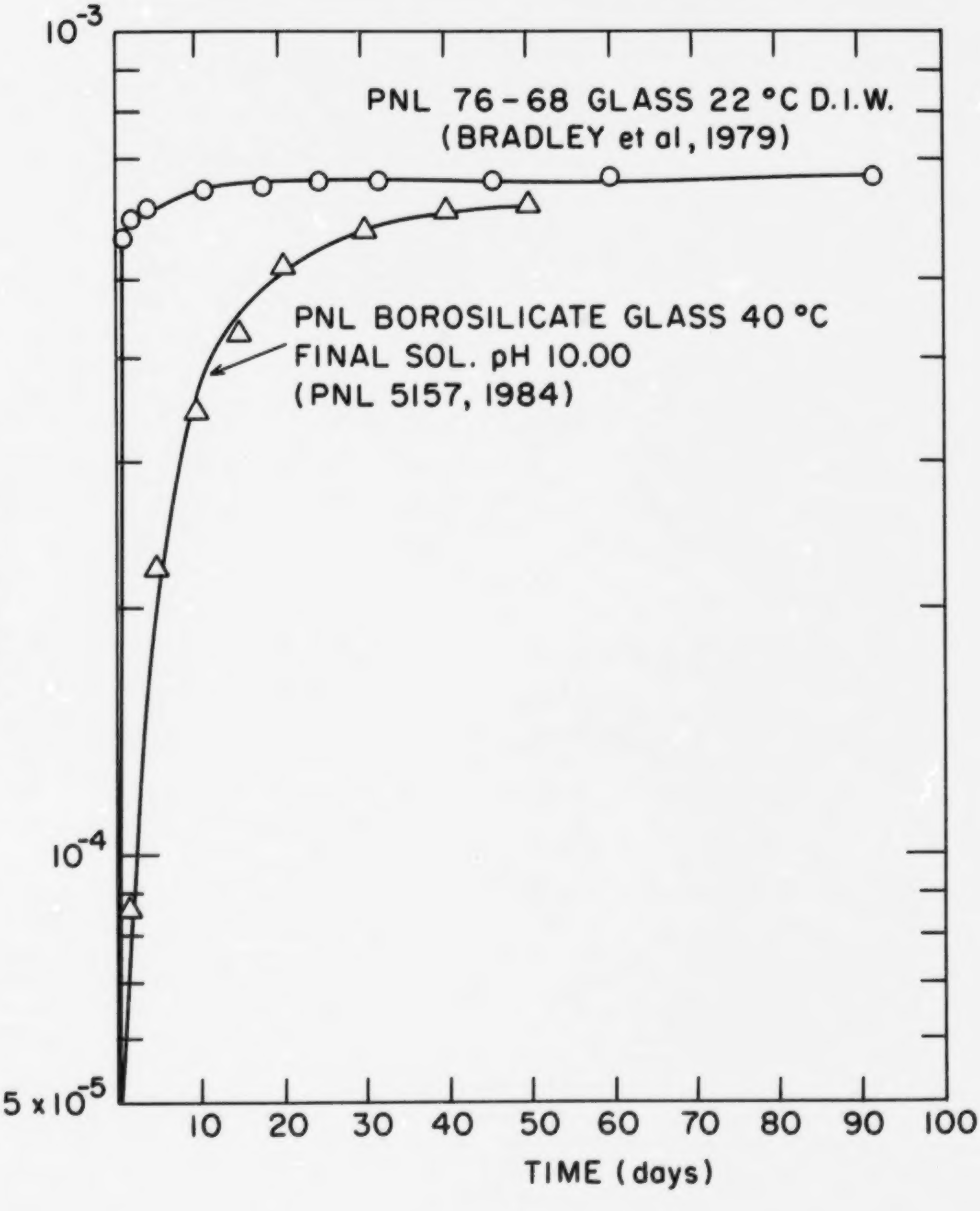

Figure 3.28 Cumulative normalized fraction of Tc released vs time.

3.2.5.1 Tabulation of Solubility Data for Tc-99

In addition to the above reviews of technetium release data, there are a few additional solubility values reported in the literature. These have been compiled and are shown in Table 3.30. In the first four references, the test-temperatures are not mentioned, so it is assumed that they are for room temperature conditions. It is clear from Table 3.30 that Eh can greatly affect the solubility values. For reducing conditions, the solubility value is quite low. However, due to radiolysis effects in a repository, the groundwater could become oxidizing. Therefore, the values given by Early (1982) and Salter (1981a) for unirradiated conditions are not likely to be conservative with respect to expected repository conditions.

Even under reducing conditions, there is some uncertainty in the solubility values reported by various workers. The range is from 10^{-10} to 10^{-5} ppm. The results reported in references Coles and Apted (1984), Bradley et al. (1979), and PNL-5157 (1984) are under oxic conditions but the Eh values are not reported.

3.3 Summary and Conclusions

In determining radionuclide solubilities, there are several critical points to be made. These are related to defining the system (solid and liquid phases) ensuring that equilibrium occurs, and selecting an adequate technique for measuring concentrations of nuclides of concern. Even supposedly identical systems can give wide disagreement in solubility results due to differences in the solid phases. If colloids or precipitates are formed, this could also cause uncertainties.

To develop a good thermodynamic data base, it is necessary to obtain the solubility product values for the various actinide compounds which are present in high level waste. For this, the solute used should be a pure stochiometric phase or a radionuclide rich end number of a solid solution. Some of the values reported in the literature are compiled in the tables for each of the radionuclide in this study by BNL.

The current review suggests that there are limited available data for the solubilities of Am, Pu, Np, U and Tc. Even the available soluibility data show uncertainties and wide variation depending on the experimental conditions and solute materials used. Americium is one of the largest contributors to the total activity of high level waste after the containment period, but there appear to be no solubility tests conducted under conditions simulating a repository environment. (See Tables 1.2 through 1.4 for estimated repository conditions for spent fuel waste packages in the post-containment period.) The reported Am solubility values varied by a factor of 6 at pH 8 to 10. For plutonium, technetium, and neptunium there is also much uncertainty in the available data. Little of the information could be used to predict controlled release rates under repository conditions. There is a significant amount of work on uranium solubility, but most of these studies were carried out at room temperature. More relevant work is still needed for uranium solubility under repository conditions.

Table 3.30 Technetium - 99 Solubility

Reference Source	Solubility (ppm)	Conditions
Table compiled by Kranskopf	10^{-3}	Not specified
(Ref. in Pigford, et al. 1983)	10^{-10}	Reducing conditions (Eh=-0.2V and pH=9.0
Early (1982) (Ref. ORNL/TM-9191/V3)	$>10^{-9}$	Groundwater under reducing conditions
Salter (1981a)	10^{-7}	Basalt groundwater under reducing conditions
Allard and Torstenfelt (Sweden, 1983)	10^{-5}	Groundwater under reducing conditions (Eh(V) < 0.27 - 0.06 pH
	10^{-1}	Groundwater under mildly oxidizing conditions (Eh(V) between 0.27 - 0.66 pH and 0.45 - - 0.06 pH)
Coles and Apted (1984)	50	Basalt groundwater under oxic hydrothermal conditions (Tc-99 doped glass and 200°C. Eh not measured)
	5.0×10^{-3}	Above plus basalt is present in the experiment
Bradley, et al. (PNL-3152, 1979)	2.21	Tc-99 doped PNL glass in deionized water at 22°C. (Eh not measured)
PNL-5157 (1984)	Tc-99 doped DWRG in deionized water under different temperatures and pH levels. These are unsaturated concentration values at the end of 50 days. Eh is not reported for those tests.	
	3.4	pH = 1, 90°C
	5.5×10^{-2}	pH = 3, 90°C
	0.17	pH = 11, 90°C
	0.18	pH = 9.6, 90°C
	3.6×10^{-2}	pH = 11, 40°C
NUREG/CR-3730 (1984)	10^{-2}	Synthetic basalt groundwater under reducing conditions by addition of hydrazine

The actinide-bearing waste forms such as glass and spent fuel are chemically complex compared to the simple oxide or hydroxide compounds usually used in many solubility studies. Also the waste form/water system may not reach thermodynamic equilibrium since several other factors may be present. For example, hydrolysis, disproportionation, colloid formation, gel formation, absorption and changes in the solid state species from metastable to stable form. Careful independent study of the changes occurring in the system with time is necessary when any of those factors which produce non-equilibrium conditions exist. Short-term determinations of solubilities should be augmented by long-term studies.

Most of the studies reviewed here approached equilibrium from undersaturation conditions. For reliable results, it should be demonstrated that equilibrium has been achieved in solubility measurements. The most rigorous method of demonstrating that a solubility experiment has reached equilibrium is to approach steady state from both undersaturated and supersaturated conditions. The value of the solubility product constant will be the same in both cases if equilibrium has been achieved.

Radiation can effect the solubility due to radiation damage to the host rock and radiolysis of groundwater. Radiolysis can produce more chemically aggressive species in the groundwater, which could effect the solubility. Also, alpha radiolysis can raise the Eh of the leachant which raises the saturation concentration of multivalent nuclides. Radiation damage to rock salt may also cause sodium colloid formation which may alter the pH of brine inclusions. Successful long term prediction of radiolysis effects will require a better data base geared towards the complex repository environment.

The groundwater chemistry also greatly affects radionuclide solubility and colloid formation. The review on plutonium suggests that the solubility data in deionized water need not be the most conservative. For plutonium, it was also found that the higher the sulfate concentration in solution, the less the plutonium solubility, while the presence of fluoride enhanced Pu solubility. For neptunium, the presence of fluoride ions in the solution did not enhance the solubility. Solubility of technetium and uranium are greatly affected by Eh; increasing the Eh causes higher solubility. The effect of Eh on Pu and Np solubilities are not very clear from this review. Americium solubility, however is little affected by Eh changes.

The presence of host rock materials and iron in some of the experiments has resulted in the formation of radionuclide bearing psuedocolloids or true colloids. True colloids are formed, when conditions develop that produce a supersaturated solution of a given radionuclide. The speciation experiments of Pu in natural groundwaters confirm the formation of such colloids. However, for all the radionuclides reviewed here, very little work has been done on the formation, composition and properties of colloids containing these radionuclides. This is an important omission since the release could occur through colloid or psuedocolloid transport.

In summary, the above review suggests that there is not enough data on radionuclide solubility and colloid formation under anticipated repository conditions. There is a wide variability in published solubilities as a function of redox conditions, groundwater chemistry, and waste material used.

3.4 Recommendations for Future Work

Solubility should be determined for radionuclides of concern using glass as well as spent fuel in experiments that simulate the likely repository environment. Tests should be conducted until the solubility limit is reached. To confirm the reliability of the data, solubility measurements should be conducted from undersaturated as well as oversaturated conditions. The mechanisms of colloid formation, the species associated with it, and the amount of colloids likely to be formed for each radionuclide should be addressed in greater detail.

3.5 References

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4. MODEL/CODE EVALUATION

Demonstration with "reasonable assurance" that regulatory criteria on canister lifetime and controlled release are met will require computer modeling of the physical processes and events that may occur. Therefore, determining the accuracy and reliability of the computer models is an important issue which must be addressed. This will require a detailed review of the computer models including an evaluation of the mathematical models embodied in the computer code; a review of the input needed by the code in terms of availability; a review of the numerical solution procedure; and whenever possible use of the computer code on test problems to highlight deficiencies in the code that are not readily apparent from evaluating the models. In most cases, much can be learned from actual "hands on" experience with the code.

The complexity of waste package performance assessment necessitates that a number of different computer codes be used. Thus, reviewing all of them will be a major task. These codes can be divided into two categories: codes which describe the entire waste package system using relatively simple models, and codes which describe a specific process which is part of waste package performance using detailed models. The results of the process specific codes are combined with each other to provide the entire system performance assessment.

The waste package system code WAPPA was reviewed (Pescatore, 1985) and here we will discuss two problems which became apparent during the review. First, it was found that the Office of Nuclear Waste Isolation, ONWI, released slightly different versions of WAPPA to NRC and BNL. A discussion of the differences and the need for quality control is presented in Section 4.1. Second, it is currently planned to rely on WAPPA in licensing calculations to predict canister corrosion, waste form leaching, and radionuclide transport in the waste package system (ONWI, 1984). However, the review of WAPPA uncovered several deficiencies which make WAPPA's predictions questionable. Section 4.2 of this report will discuss some general requirements for licensing computer codes and apply these requirements to WAPPA.

Attempts to perform detailed reviews of the computer codes TEMP, a thermal analysis code, and BRINEMIG, a brine migration code, were limited by the inability of BNL to obtain these codes from ONWI. Both of these codes were used in the waste package performance analysis presented in the seven salt Environmental Assessment reports. Further, the salt performance assessment plan (ONWI, 1984) states that peer review is an important process and that all codes would be released to NRC for independent review and testing. Sections 4.3 and 4.4 present a cursory review of TEMP and BRINEMIG respectively as obtained from the minimal documentation released on these codes.

4.1 Differences Between WAPPA Source Programs Separately Transmitted to BNL and NRC

In June 1983 the computer program WAPPA, two test problems, and the data necessary to run these problems were sent to BNL on a tape from ONWI. The version of WAPPA contained on the tape was Revision 0 with a quality assurance number (variable QACIN in the code) 420--20C-02. In December, 1983, BNL received a letter form update which revised portions of the code and the quality assurance number was changed to 420--20C-02B. Independently, the NRC received a tape transmitted in November 1983 containing the WAPPA code Revision 0 apparently with quality assurance number 420--20C-02B.

This section of the report discusses differences in the files catalogued on the two tapes, differences in the BNL and NRC version of WAPPA, and comments on the need for quality assurance with computer codes.

4.1.1 Differences in Files Catalogued on the Two Tapes

The first obvious difference between the information supplied to BNL and NRC is that the tapes contain a different number of files. The tape given to BNL has 28 files and the NRC tape has 19 files. The reason for the discrepancy is that the BNL tape has four test problems with output files for each problem whereas the NRC tape has only one test problem with one output file. Also, the BNL version along with the entire source listing has the code divided into six segments representing the process models. The NRC version has only the source listing.

For ease of reference, the list of files from each tape is included in Appendix A. It is important to notice that the quality assurance number on the BNL tape is 420--20C-02 whereas on the NRC tape it is 420--20C-02B.

The other discrepancies between the tapes occur because the NRC tape has files that highlight the differences between the 420-20C-02 and 420--20C-02B versions of WAPPA and differences between CDC machine and VAX machine versions of WAPPA. These files can be extremely useful in tracing the history of the code.

In addition to these comparisons it would be desirable to produce a file with a comparison of the output of the sample problem on both the old and new versions of the code. If there are no differences in the output, a new problem that demonstrates the influence of the changes should be computed to show that the changes are working correctly.

4.1.2 Differences Between the Source Code Supplied to BNL and NRC

To examine the differences between the versions of WAPPA on the tapes supplied to BNL and NRC a computer program written by Ms. Judy Colman of BNL which performs a line by line comparison of two files was used. To ease the process, non-executing comment statements were removed from the comparison checks.

As a result of this check it was determined that there were differences on a few hundred of the approximately 12,000 statements that form WAPPA. This is partially explained by the fact that BNL had the version with quality assurance number 420-20C-02 whereas NRC had 420--20C-02B. However, adding the corrections to the BNL file supplied by ONWI theoretically should have made the BNL and NRC files identical since they were both given the same quality assurance number. In fact, there were still differences on roughly 100 statements.

The majority of these discrepancies arise due to changing the format of output statements or spacing in common blocks and do not effect the operation of the code. However, there are eight or nine differences in statements that could possibly alter the codes performance. These differences are described in detail in Appendix B.

The cause of the differences between the NRC version and the letter form updated BNL version fall into three categories: errors of omission, errors in transmission, and errors in translation. Errors of omission refers to several instances in which the letter form update did not contain modifications found in the tape version. Errors in transmission refers to typographic errors or illegible instructions in the letter form update. In a few cases, statements differ by one character; for example the NRC version may have a comparison based on some variable being greater than or equal to another variable, and in the BNL version the comparison is based on the first variable being strictly greater than the second variable. Errors in translation refer to mistakes in converting the letter form update to computer code and include misinterpretation of the letter and typing errors. It should be recognized that the update instructions supplied to BNL corresponded to a version of WAPPA operating on a VAX computer; however, BNL has a CDC computer system and it required several phone calls to ONWI to clarify how to incorporate the changes into the CDC version of WAPPA.

As an auxiliary check on the source code, the BNL version of WAPPA was compared with the source listing provided on microfiche with the WAPPA code manual (Intera, 1983) as both had the same quality assurance number. Although a line by line comparison was not feasible, comparison at all segments where the BNL and NRC versions differed plus a few randomly chosen segments of the code did not produce any differences between the BNL and WAPPA code manual listing. Apparently, these two listings are identical.

4.1.3 Conclusions

The fact that there are several inexplicable discrepancies between the same quality control number version of the WAPPA code indicate a need for better quality control.

4.1.4 Recommendations

- The version of WAPPA is defined by both the revision and the quality assurance number. Both should be prominently displayed in the comments at the beginning of the code. Currently only the revision is displayed at that location. Thus, at first glance the BNL and NRC version appear to be identical since they are both revision 0.

- The date that the most recent quality assurance number was incorporated into the code should be displayed in the output and in the comments at the beginning of WAPPA. There were substantial changes made to WAPPA between June (BNL version) and November (NRC version) of 1983. Yet, the date listed for both codes is February 25, 1982. Again, this leads the casual observer to believe the BNL and NRC versions are identical.

- When a new version of a code has undergone the checks necessary for quality assurance, a master tape of the code, its associated data files and test problems should be made. All future releases of this version of the code should be copied directly from this master tape. This will not guarantee the accuracy of the code but will insure consistency of each released version of the code.

- Letter form updates to existing versions of a code should be avoided whenever possible. There are too many sources for error in this process. Updates should be supplied through tapes. If it is necessary to release updates in letter form, the letter should contain a statement which explains that there is no guarantee that the changes in the letter will reproduce the quality controlled version of the code. Codes updated by letter should not be used for licensing calculations unless it can be shown that the code revisions have been performed properly and the code is identical to the quality controlled version.

- The choice of the version of WAPPA which should be used if NRC decides to make independent calculations with this code is difficult because of the inconsistencies between the different versions. Ideally, NRC should wait until DOE releases an updated version of WAPPA before performing calculations. However, the release of an updated version of WAPPA is not imminent and NRC may decide to use an accessible version of the code. If this is the case, the version obtained by NRC in November, 1983 with quality assurance number 420--20C-02B is the most recent tape-transmitted version and, therefore, is a slightly better choice than either BNL version. When DOE releases a new version of WAPPA, it should be compared with the current version and the differences noted before using the updated version.

4.2 Requirements for Licensing Computer Codes Used in High Level Waste Repository Performance Assessment and Application to the Code WAPPA

Computer simulation of the behavior of high level waste repositories is recognized as a necessary method in demonstrating with reasonable assurance that NRC criteria on repository performance can be met. However, before DOE uses a computer code for licensing calculations it should be reviewed for its technical content, verified, validated and demonstrated to be acceptable to the NRC. There are a number of NRC documents that give guidance on the requirements that must be met by a computer analysis to satisfy the NRC (Sillings, 1983; NRC, 1984; Knapp, 1984). However, these guidelines are general in nature and are not directed at any code in particular. The following sections of this report provide six general requirements for licensing of a code and relates these requirements to the computer code WAPPA.

4.2.1 Failure Modes and Effects Analysis (FMEA)

To obtain an overview of potential problems in repository performance the NRC should require the DOE to conduct a failure mode and effects analysis. This is a subjective analysis which identifies all possible methods of repository failure. As part of the analysis the DOE should define and document the procedures that will be used to examine the various failure modes. A FMEA will benefit the DOE because it will provide guidance as to which analytical and computational techniques need further improvement and will help insure that all identified failure modes are analyzed.

When computational analysis is recommended for a given failure mode the DOE should identify which code(s) will be used for the analysis. This list will help describe the role of each computer code in repository performance assessment. A FMEA would highlight the fact that the code WAPPA will play a major role in waste package performance assessment in salt repositories because it models many near field processes and is the only code identified as being capable of modeling canister and overpack corrosion.

When the DOE attempts to obtain NRC approval for use of a code in support of licensing a repository they should provide a list of failure modes addressed by the code and discuss the role the code plays in performance assessment. This information could be contained in the code manual. As a minimum the manual should describe the types of problems for which the code has been verified and/or validated.

4.2.2 Identify Type of Code Analysis

Along with the type of problem, (leaching, groundwater chemistry etc.), the type of analysis that a code will perform must be specified. That is, identify which of the following the code will be used for: screening possible failure modes, sensitivity analysis to determine the key parameters, probabilistic analysis to estimate uncertainties in predictions, or deterministic analysis for best estimates, upper bounds, and repository design calculations. The use of the code will influence its acceptability to the NRC. For example, a code used only for screening calculations would not have to be as accurate as a deterministic code that performs licensing calculations.

It has been suggested that WAPPA could be used for any of the four types of analysis. However, current use of WAPPA by the DOE has focused on deterministic analysis for best estimates of waste package performance to support the choice of a salt geology as a potential repository site (Jansen, 1984).

4.2.3 Review of the Computer Code and Associated Documentation For Technical Content

Preferably, after the uses of the code have been identified, it must be reviewed for its technical adequacy. This will entail review of the mathematical models, their associated equations, numerical solution procedure, and overall system logic in terms of how well the code represents the physical system being modeled and the level of accuracy required for consistency with the potential uses of the code.

The code documentation should follow the guidelines presented in the Draft Technical Position on Documentation of Models (Sillings, 1983). This document was written specifically for high level waste repository assessment codes. In general, the code documentation should allow the users to successfully operate the code, justify the models used in the code, describe the range of applicability and limitations of the models, inform the user which models, code options, and boundary conditions have been verified, and describe any test problems which have been used to validate the code or any portion of the code.

The code WAPPA and its documentation (Intera, 1983) has been reviewed (Pescatore, 1985) for technical adequacy. As a result of this review several suggestions were made (Pescatore, 1985; Sullivan, 1985) to improve some models, provide better justification for others, and upgrade the documentation to conform to NRC guidelines (Sillings, 1983). In the form reviewed it would be difficult, perhaps impossible, to approve WAPPA for licensing calculations.

4.2.4 Review Code Usage In Failure Mode Analysis

For complicated problems such as repository performance assessment, analysis of a given failure mode will often require sequential or simultaneous use of several computer codes.. Thus, the complete analysis procedure must be reviewed to assure that the system of computer codes properly models the failure mode.

Part of this review will involve examination of the interaction between various computer codes. For a specific code it must be demonstrated that input from other codes in the process falls within the range of applicability of the code and this input will allow reliable and accurate predictions for use in the rest of the analysis.

WAPPA is a systems code that will require a number of auxiliary codes to provide the boundary conditions for temperature, pressure, groundwater chemistry and flow rate. Thus before licensing approval for WAPPA can be given, it must be demonstrated that the auxiliary codes identified to supply the boundary conditions must be compatible with WAPPA and the propogation of errors in the boundary conditions on WAPPA's predictions must be examined. For example, a one degree error in the boundary temperature leads to a one degree error in the temperatures calculated by WAPPA. This, in turn, leads to errors in the prediction of temperature dependent processes like corrosion and leaching.

4.2.5 Demonstrate the Code Is Reliable and Accurate

After defining the role of a computer code in performance assessment it must be shown that the code can accurately and reliably predict a solution to the class of problems that it will be used to study. This can be demonstrated through verification and whenever possible validation.

Verification is defined as "assurance that a computer code correctly performs the operations specified in a numerical model"(Knapp, 1984). It can be achieved through comparison with: hand calculations, analytical solutions, other verified computer codes, and standard benchmark problems having known solutions. For complex codes it is not practical to verify every option or combination of options. Thus, careful documentation of the specific options, boundary conditions, and range of parameters that the code has been verified on is necessary.

Validation is defined as "assurance that a model as embodied in a computer code is a correct representation of the process or system for which it is intended" (Knapp, 1984). Validation can be accomplished through comparison with accepted experimental results. Again, validating every option is not practical and documentation of the problems that the code has been validated against is important and necessary.

Waste package performance assessment codes have the difficult task of predicting the behavior of many interactive physical processes over a time span of thousands of years. Coupled with this there are large uncertainties in some of the physical parameters that will comprise the data base required for analysis and there will be no long term (repository lifetime) data available. Thus, validation on problems that represent repository conditions will be difficult if not impossible. In this case, validation will have to be achieved on short term (up to several years) data. In cases where validation is not possible, extensive verification and model justification will be required. Complicated benchmark problems designed to test the code may prove extremely useful in this situation.

Even if a code has been verified and validated over a range of conditions this does not guarantee that the predictions of a code accurately reflect the physical processes being modeled. However, verification and validation do increase the confidence in the code.

Thus, an extremely important and difficult question is, when has it been demonstrated that enough confidence can be placed in a code to allow its use in licensing calculations? It is expected that there will be no set rules as to the extent of verification and validation required and that peer review and expert opinion will be necessary to satisfy licensing requirements. Peer review and expert opinion have been used as the cornerstone for licensing nuclear reactor safety codes.

As a minimum for licensing, all major options likely to be used during repository assessment calculations must be verified and, to the extent practible, verification should be conducted over the range of environmental conditions likely to be encountered during the lifetime of the repository. Validation of the code against available experimental data is also necessary. Preferably, validation of the entire code against a given experiment will be possible. However, if this is not the case, as in a systems code like WAPPA, the models should be validated individually. Finally, the NRC should be allowed to specify any problem that falls within the postulated domain of code validity as a test problem. Satisfactory performance of the code is required for approval for licensing calculations.

Demonstration that the code WAPPA is reliable and accurate will be an extremely difficult task. WAPPA is a systems code that has models for radiation, thermal, mechanical, corrosion, leaching and transport processes.

Currently, there are no experiments that combine all of these processes and, therefore, validation of WAPPA as a unit is impossible. Furthermore, WAPPA is unique in that it is the only code that models all of the aforementioned aspects of waste package performance. Thus, benchmarking against other codes is not possible. Finally, development of a problem with a known solution which tests all of WAPPA's models will be difficult. Thus, for lack of a better alternative, WAPPA's models will have to be verified and validated on an individual basis. In some instances, it may be possible to verify a few models simultaneously and this should be done. It should be recognized that individual model verification does not account for synergistic effects between models.

Individual verification of WAPPA's process models should be straight forward as the modeling is empirical and simplistic in nature. Thus, hand calculations should be relatively easy to perform. However, because the modeling is empirical rather than mechanistic, validation against a given experiment may be more dependent on the proper choice of data than anything else. Thus, for a different data set, WAPPA may no longer provide a good representation of the physical system.

4.2.6. Quality Assurance Plan

In general, enforcing a good quality assurance program which entails careful documentation and review in order to have accurate records of the work that has been done and to minimize the number of errors in a computer program is a worthwhile practice for a number of reasons.

First, in many cases, the cost of maintaining a computer code in operational form often exceeds the development cost. One reason for this is that correcting errors in existing codes and reperforming previous calculations is time consuming and expensive.

Furthermore, the predictions resulting from the use of computer codes to support licensing of a repository will receive intense review by a number of interested parties. This review may occur several years after the code development and use has been performed. In this time, personnel that originally performed the work may no longer be available to explain the work. Thus, careful documentation and retrievability of computer codes over their life span is necessary to assure the quality and reliability of the computer calculations.

Continued refinement and testing of a computer code will lead to discovery of errors in earlier versions of the code. These errors are to be documented with an explanation of the potential ramifications with respect to previous predictions, corrected in all versions of the code, and may necessitate reanalysis of problems used to support licensing decisions. Therefore, retrievability is again an important component of a quality assurance program.

Attaining the capability to retrieve any version of a computer program will require the code developer to periodically document and permanently store the code. Later, this version of the code must not be altered except to correct errors in coding and these changes must be documented. Improvements to the code should be incorporated into a new version of the code.

4.2.7 Summary

The following six steps have been identified as requirements for licensing computer codes used in repository assessment calculations:

1. Failure modes and effects analysis,
2. Identify type of code analysis,
3. Review the computer code and associated documentation for technical content,
4. Review code usage in failure mode analysis,
5. Demonstrate the code is reliable and accurate,
6. Quality assurance plan.

This section has described these requirements and has used the code WAPPA as an example of how they could be applied to a specific computer code.

As a word of caution, even if a computer code has been approved for licensing calculations, each use of the code must be critically reviewed. Specifically, the data used in the models must be justified (this is especially important for codes that rely heavily on empirical models such as WAPPA) and an estimate of the confidence in the predictions must be given. Whenever possible the confidence in the code should be quantified in terms of a range of uncertainty in the predictions. This analysis should consider uncertainties in the data, the modeling, and completeness of the models.

4.3 Review of TEMP

TEMP is a computer code which calculates the three-dimensional time dependent temperature field arising from a series of finite-length line sources of heat. It has been used in waste package analysis for the Environmental Assessment reports to supply the time dependent temperature boundary condition for WAPPA and the spatial and temporal evolution of temperature required to calculate brine migration in BRINEMIG.

TEMP is based on obtaining an integral solution for the heat conduction equation from a single finite-length line source in an isotropic homogeneous medium of constant thermal diffusivity. To obtain the temperature at a given point, the integral solution is obtained through numerical approximation of the integral and contributions at that point from all line sources in the repository are summed. Summation is possible due to linear superposition that applies if the thermal diffusivity is constant.

It is well known that the thermal conductivity of salt varies with temperature which itself varies with spatial position. To partially remove this limitation, a transform of the heat conduction equation is made.

$$\rho c \frac{\partial T}{\partial t} = \sum_{i=1}^{3} \frac{\partial}{\partial x_i} k \frac{\partial T}{\partial x_i} \qquad (4.1)$$

where ρ = salt density,
c = salt heat capacity,
T = salt temperature,
k = thermal conductivity, and
$\sum_i$ = summation over all three dimensions.

Multiplying both sides by k and integrating over temperature gives:

$$\int_{To}^{T} k\frac{dT}{dt} = \int_{To}^{T} \frac{k}{\rho c} \sum_{i=1}^{3} \frac{\partial}{\partial x_i} k \frac{\partial T}{\partial x_i} \quad . \qquad (4.2)$$

Defining the transform variable,

$$\phi = \int_{T_o}^{T} k \, dT, \qquad (4.3)$$

and thermal diffusivity,

$$\alpha = k/\rho c,$$

yields:

$$\frac{\partial \phi}{\partial t} = \int_{T_o}^{T} \alpha \sum_{i=1}^{3} \frac{\partial}{\partial x_i} k \frac{\partial T}{\partial x_i} \qquad (4.4)$$

TEMP now assumes that the thermal diffusivity is independent of temperature now giving:

$$\frac{\partial \phi}{\partial t} = \alpha \sum_{i=1}^{3} \frac{\partial^2 \phi}{\partial x_i^{\,2}} \qquad (4.5)$$

The reason for this assumption other than mathematical convenience is not clear. In the discussion of TEMP (McNulty, 1984) it is stated that only minor variations in density and heat capacity are expected over the range of repository temperatures; however, the basis for the transform is the temperature dependence of thermal conductivity. Thus, one must expect the thermal diffusivity to change.

Looking at Eqn. (4.4) in more general terms, one can write the thermal diffusivity as:

$$\alpha(T) = \alpha_o + \Delta\alpha(T) \qquad (4.6)$$

where α_o = average thermal diffusivity, and

$\Delta\alpha$ = variation about the average.

Using this in Eqn. (4.4) gives:

$$\frac{\partial\phi}{\partial t} = \alpha_o \sum_{i=1}^{3} \frac{\partial^2\phi}{\partial\chi^2} + \int_{T_o}^{T} \Delta\alpha \sum_{i=1}^{3} \frac{\partial}{\partial\chi_i}\, k \;\frac{\partial T}{\partial\chi_i} \qquad (4.7)$$

From Eqn. (4.7) it is clear that TEMP ignores the temperature dependent variation of thermal diffusivity about an appropriately selected average. Provided the variations are small relative to the average this will be a good approximation.

TEMP has been validated against analytical solutions and the finite difference code HEATING5 for the problem of a single infinite line heat source and constant physical properties. The calculation of temperature when there is a variation of thermal conductivity was supposedly validated against the finite difference codes HEATING5 and HYDRA. However, the documentation on this problem has not been released.

4.3.1 Limitations of TEMP

- Physical properties are assumed to be independent of position. This ignores the local variability due to impurities expected in a repository and, more importantly, does not allow detailed modeling of the waste package which will have very different physical properties. Thus, temperature predictions in the vicinity of the waste form, canister, overpack, and backfill (if any) are open to question. This suggests that TEMP may not be adequate to supply input for waste package performance codes like WAPPA and BRINEMIG.

- As discussed earlier, TEMP will be accurate if variations in thermal diffusivity about its average are small. The non-linearities resulting from variations in thermal conductivity also cause the superposition method to be invalid.

- The predictions from TEMP are only as good as the input data. Currently, the in situ thermal conductivity is not well known. Careful site characterization is needed to correct this problem.

- Radiative heat transfer is not considered. Salt is transparent in the infrared, and radiative heat transfer may be important.

4.3.2 Advantages of TEMP

Due to its analytical solution procedure the TEMP code has many advantages over traditional finite difference codes. In particular, given a position in space and the time, the temperature is obtained through integration. In contrast, finite difference codes must repeatedly solve the heat conduction to obtain the time evolution of the temperature field. Thus, TEMP is faster and does not require the code user to consider numerical errors introduced by the choice of spatial mesh or time step.

4.3.3 Conclusions

TEMP is an efficient method of obtaining the temperature at a given spatial location and time. Thus, it may be useful in screening and sensitivity studies. Before accepting TEMP's prediction for near field temperatures it must be shown that local inhomogeneities caused by natural variations in the lithology, the repository rooms, shafts, and boreholes, and most importantly the waste package, have only a minor influence on the temperature. Due to lack of repository data, the only way to demonstrate the accuracy of TEMP is by comparison to more detailed numerical codes which can accomodate spatially varying physical properties. Finally, to determine the accuracy of the numerical integration procedure in TEMP would require the acquisition of better documentation and the code for testing.

4.4 Review of BRINEMIG

The solubility of salt in a brine inclusion increases with temperature. Therefore, when a thermal gradient is applied across the salt, dissolution of salt into the brine occurs at the hottest end of the inclusion. This causes supersaturation of the brine and precipitation of the salt at the cooler end. Thus, the brine inclusion migrates up the temperature gradient within a single salt crystal. This mechanism will cause brine to migrate towards the waste package.

Depending on the size of the inclusion and the number of dislocations in the salt crystal structure, brine migration can be controlled by either diffusion of the salt from the hot to the cold end or the kinetics of dissolution and precipitation. When there are few dislocations, the dissolution and precipitation steps are rate controlling and the migration velocity has been shown (Olander, 1984) to be proportional to the square of the temperature gradient. When dislocations are abundant, diffusion is rate controlling and the migration velocity becomes proportional to the temperature gradient. In both situations, the proportionality factor is a function of the local environment and the properties of the salt. In general, the proportionality factor for diffusion control is much greater than when dissolution processes are rate limiting. Thus, the inclusion velocity is much greater when diffusion is the rate limiting step, even though it is less sensitive to changes in the temperature gradient.

4.4.1 Migration Velocity

BRINEMIG was developed to predict the migration rate and amount of brine that will reach the waste package. To accomplish this BRINEMIG requires as input the initial moisture content of the salt and the spatially varying temperature field. Using these, the intracrystalline migration velocity of brine inclusions are calculated using the Jenk's equation (Jenks, 1981):

$$\log [v/\nabla T] = 0.00656T - 0.6036 \qquad (4.8)$$

where v = local velocity of brine migration,
∇T = local temperature gradient, and
T = local temperature.

After obtaining the spatially varying velocities a simple mass balance is performed to calculate the brine current.

This modeling is very simple and ignores the fact that migration velocity is dependent on inclusion size, brine composition, and the density of dislocations in the salt crystal (Olander, 1984). To compensate for these short comings the empirical Jenk's equation was developed to provide the maximum intracrystalline migration velocity based on a number of experimental measurements in which diffusion was the rate limiting process. However, the reliability of this equation has been criticized (Roedder, 1982) because of lack of data to validate the model. This is especially true at temperatures greater than 50°C. In general, there is no attempt to estimate the uncertainty associated with using the Jenk's equation to determine maximum velocity.

As a feature of BRINEMIG, there is a threshold temperature gradient below which the migration velocity is zero. This threshold gradient is predicted theoretically (Pigford, 1982; Olander, 1984) and is a function of inclusion size. However, there is some dispute on its validity (Roedder, 1982). It is suggested that the threshold gradient be set at 0.125°C/cm (Jenks, 1981); however, this is probably too high for the expected distribution of inclusion sizes and temperatures (the threshold gradient decreases with increasing temperature) at the WIPP site (Chou, 1983). Until the data firmly support the existence of a threshold gradient, it should be set to zero for conservatism.

4.4.2 Initial Water Content of the Salt

As input, the user must supply the volume percent of water in the salt. There is a wide range of water content in salt and it is not uncommon to have one or two orders of magnitude difference in water content within a given site. To overcome this problem, a conservatively high value for water volume must be used. In bedded salts, measured water content based on fluid inclusions, and not including hydrous minerals, has been shown to range up to

1.7 wt% with an average value of 0.36 wt% (Roedder, 1982). In domal salts, the water content is lower than in bedded salts and is probably less than 0.2 wt%. However, anomalous "wet zones" have been found in many Louisiana salt domes where the water content may reach 0.5 wt% (Roedder, 1982). In the salt Environmental Assessment reports, a value of 5 volume per cent (≈1.9 wt%) water was used for bedded salt sites and 0.5 volume per cent (≈0.19 wt%) water was used for domal salt sites.

4.4.3 Other Limitations of BRINEMIG

BRINEMIG assumes that the salt is homogeneous and isotropic, the one-dimensional approximation ignores end effects, the influence of radiation and thermally enhanced damage to the salt is ignored, and migration along grain boundaries is assumed identical to intracrystalline migration. There is no theoretical justification for this last assumption and in fact the transport mechanisms are expected to differ.

Also, calculations using BRINEMIG show large oscillations in the predicted spatial concentrations of brine concentration. These are probably due to numerical problems in the solution procedure and highlight the need for careful verification and validation of the code.

4.4.4 Conclusions

There is a wide variability in measured migration velocities and water content in salt. Currently, the data are not detailed enough to support an accurate, reliable calculation of brine migration. Thus, better data should be obtained through detailed site characterization. Currently, conservative, bounding calculations of brine migration are all that can be supported by the data. The computer code BRINEMIG is a simple empirical approach at calculating brine migration and can provide conservative estimates provided the initial water content is set high enough, there is no temperature gradient threshold to migration, and the other limitations previously mentioned are addressed. The best way to assure that the calculation is conservative would be through extensive verification and validation by DOE and a more detailed peer review.

4.5 Conclusions and Recommendations

Code and model evaluation conducted during this period has focused on three computer codes used in waste package performance assessment: WAPPA a waste package systems code, BRINEMIG a code that predicts brine migration due to thermal gradients, and TEMP a code that predicts the three dimensional temperature field in a repository.

The process models in WAPPA have been reviewed previously (Pescatore, 1985) and thus questions regarding WAPPA have focused on quality control and applicability of using WAPPA in licensing calculations.

Quality control on WAPPA was judged through comparing a version of WAPPA released to BNL and updated by letter and a supposedly similar version released to NRC. The comparison found several differences in executing statements indicating a need for better quality control. Letter form updates were singled out as a particularly error prone method for transmitting changes to a code.

Current performance assessment plans (ONWI, 1984) rely heavily on WAPPA. Thus, it must be shown that WAPPA is capable of accurately and reliably calculating the results for the class of problems for which it will be used. However, before developing a procedure to review a single code it was felt a general framework for assessing the usefulness of any computer code in performance assessment should be developed. This framework acknowledges the fact that performance assessment will require the use of a number of process specific codes in conjunction with each other and took the position that review of any code should be done in terms of its specified use in the overall assessment plan.

The plan is based on the following points :

- NRC should require a failure modes and effects analysis to identify all reasonable failure modes.
- The type of code analysis (screening, sensitivity, probabilistic, deterministic) needs to be specified.
- The computer code and documentation need to be reviewed for technical content.
- The usage of the computer code in the failure mode analysis needs to be reviewed.
- The code must be shown to be reliable and accurate, through verification and validation.
- A computer code quality assurance plan needs to be enforced to enable any reviewer to follow the code history .

Suggestions on how to apply these points to WAPPA were given.

A brief review of the TEMP code was performed. The analytic nature of the solution procedure offers the advantages of computational speed and ease of use, over traditional finite difference methods. However, the assumption of a homogeneous, isotropic medium with constant thermal diffusivity may limit accuracy in the very near field (i.e. waste package region). TEMP was used in the Environmental Assessment reports to provide the very near field temperature required by other codes in the analysis. Before accepting this procedure, verification of TEMP through comparison with detailed numerical codes on complicated test problems that simulate the repository geometry and environment are necessary.

A brief review of the BRINEMIG code was performed. Due to lack of understanding on migration along grain boundaries and lack of data on intracrystalline migration a mechanistic view of brine migration cannot be developed at this time. BRINEMIG attempts to circumvent this problem by using an empirical correlation which gives the maximum migration velocity. Because of the uncertainty involved in modeling brine migration, and in the assumptions made to derive the correlation, a thorough peer review of BRINEMIG is needed.

Below are listed recommendations with respect to modeling:

- NRC should enforce a quality assurance plan for computer software. Recently DOE has begun to do this, but the results of their efforts have not been released.
- Letter form updates for codes should be accepted only as a last resort. All modifications to a code should be transmitted through a quality controlled tape.
- NRC should develop a plan by which codes can be reviewed in terms of their use in performance assessment.
- NRC should vigorously attempt to obtain the computer codes planned for use in the performance assessment in order to enhance detailed reviews of these codes.

A significant amount of knowledge was gained by actual use of WAPPA. Up to this time, DOE has been uncooperative in releasing codes.

4.6 References

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5. STRESS-CORROSION CRACKING TESTS ON CONTAINER MATERIALS FOR A TUFF REPOSITORY

5.1 Introduction

The Nevada Nuclear Waste Storage Investigations (NNWSI) program is evaluating austenitic stainless steels as the prime candidate materials for high level nuclear waste containers (Russel, E. W., 1984; Juhas, M. C., 1985). Specifically, Type 304L stainless steel (SS) is adopted as the reference material with Type 316L SS, Type 321 SS, and Incoloy 825 as alternates. A high level waste container made from any of these alloys will be exposed to a tuff repository environment which includes superheated steam during the first few hundred years. In the event of the ingress of very large quantities of water or in the later part of repository life time, boiling water conditions can exist at the container surface. For the satisfactory performance of a waste package, it is expected that the container will remain unbreached by corrosion for 300 to 1000 years.

Although there is no information available on the composition of groundwater or steam that will be present in the proposed unsaturated zone of the tuff repository, the groundwater chemistry is thought to be similar to the reference J-13 groundwater composition given in Table 5.1. The general corrosion resistance of the candidate alloys in this water at ≈100°C is stated to be small (UCRL-89988, 1983), but the available information on localized corrosion such as pitting, crevice or stress corrosion under the complete range of repository conditions is uncertain. For example, a survey of the literature on stress-corrosion cracking (SCC) behavior of austenitic stainless steels in relatively pure steam/water/air environments suggests that the presence of a few ppm of Cl^- and O_2 are sufficient to cause stress-corrosion cracking (BNL-NUREG-51630, Vol. 6, 1984). In fact, recent Japanese experiments on a range of stainless steels and high nickel alloys in boiling deionized water confirm that, even under such benign conditions, stress-corrosion cracking occurs (JAERI-M-82-145, 1983). In that study, double U-bend specimens were used and cracks usually developed on the inner specimens, thus indicating enhancement of SCC under crevice conditions. Type 304 and Type 304L SS exhibited SCC behavior in the absence of radiation and also under a gamma dose rate of 1.1×10^5 R/h.

The observations briefly mentioned above and reviewed in a previous report (BNL-NUREG-51630, Vol. 6, 1984) suggest that the candidate alloys may be susceptible to SCC under tuff repository conditions. Therefore, a test program has been initiated to evaluate the SCC susceptibility of Types 304L, 316L, 321 stainless steel, and Incoloy 825, in a simulated repository environment. Since there is little information available on the properties of groundwater that would come in contact with the waste package, an exploratory experiment is also included in the test program to assess the chemistry of water reacted with crushed tuff. The present report describes the progress made under this program since the publication of a previous report (BNL-NUREG-51630, Vol. 6, 1984).

Table 5.1 Reference groundwater composition for tuff repositories (based on composition of water in Jackass Flats Well J-13 at the Nevada Test Site).

	Concentration (mg/liter)
Lithium	0.05
Sodium	51.0
Potassium	4.9
Magnesium	2.1
Calcium	14.0
Strontium	0.05
Barium	0.003
Iron	0.04
Aluminum	0.03
Silica	61.0
Fluoride	2.2
Chloride	7.5
Carbonate	0.0
Bicarbonate	120.0
Sulfate	22.0
Nitrate	5.6
Phospate	0.12
pH - slightly basic (7.1).	

5.2. Experimental Method

The stress corrosion susceptibility of Types 304L, 316L, and 321 stainless steels, and Incoloy 825 under simulated tuff repository condition is being evaluated using the C-ring method (ASTM, 1979). A brief description of the test method is given below, but the details of the testing apparatus, procedure and materials used can be found elsewhere (BNL-NUREG-51630, Vol. 6, 1984).

C-ring specimens with V-notches at the apex were fabricated from seamless 0.75 inch o.d. x 0.125-inch wall tubing for the stainless steels and 0.84 inch o.d x 0.109 inch wall tubing for the Incoloy. Each alloy is tested in the as-received (solution annealed) as well as heat-treated (sensitized) conditions. During the sensitization treatment the tubing was maintained at 600°C for 100 hours followed by furnace cooling. A comparison of microstructures of the as-received and heat-treated specimens shows that the heat treatment has sensitized the stainless steels by precipitating carbides at the grain boundaries. The sensitization is more prevalent near the surface than in the middle of the specimens. In the case of Incoloy 825, the heat treatment mostly resulted in the precipitation of second-phase particles (probably TiC).

The notched C-ring specimens (used in triplicate for each test condition) are stressed using stainless steel nuts and bolts to give a stress at the apex equal to 90% of the elastic limit for an unnotched sample. Due to stress concentration effects at the notch root and the reduced area of cross section under the notch, however, some plastic strain is introduced in the specimens.

The stressed specimens are tested in synthetic J-13 and ten-times concentrated J-13 water in the presence of Topopah Spring crushed tuff. The use of the concentrated solution represents the situation when salts, precipitated after evaporation of groundwater, are redissolved in cooler water subsequently percolating towards the repository horizon. The specimens, surrounded by crushed tuff, are placed in boiling liquid and the steam above it.

A total of 288 specimens are included in six parallel tests which last for-3-, 6- or 12-month durations as shown in Table 5.2. The pH of the test solutions is measured every month. At the end of a test 50 mL of solution is withdrawn from the vessel and mixed with 50 mL of boiling distilled water. The solution is then cooled to room temperature and filtered through a Whatman 42 paper. Another 100 mL of test solution is cooled to room temperature and filtered without dilution. The chemical compositions of test solutions have been determined using standard analytical

Table 5.2 Test matrix for stress corrosion of candidate stainless steels and Incoloy-825.[a]

Sample Condition	Exposure Medium[b]	Total Exposure Time and Number of Samples		
		3-Month	6-Month	12-Month
Solution Annealed (SA)	J-13 Steam	3	3	3
SA + Sensitized	J-13 Steam	3	3	3
SA	J-13 Water	3	3	3
SA + Sensitized	J-13 Water	3	3	3
SA	(J-13 Steam)X10[c]	3	3	3
SA + Sensitized	(J-13 Steam)X10	3	3	3
SA	(J-13 Water)X10	3	3	3
SA + Sensitized	(J-13 Water)X10	3	3	3

[a] This test matrix comprising 72 samples constitutes the tests on one of the four candidate materials. An identical matrix will be used for all eight materials and the total number of all specimens tested will be 288.

[b] All tests are conducted in the presence of crushed tuff.

[c] This environment is the steam/air phase above 10X concentrated J-13 well water.

techniques. A comparison of the chemical analyses of the dilute and the normal strength test solution would indicate if any precipitation occurs during cooling to room temperatures. After the solution samples are collected, the test vessel is cooled to room temperature and the C-ring specimens are examined for cracks. Representative specimens are cleaned ultrasonically in distilled water and then examined under an optical or scanning electron microscope. The cross sections of a few specimens cut perpendicularly to the notch were also examined for any microscopic cracks.

5.3 Results To Date

5.3.1 Stress Corrosion Cracking Tests

An optical microscope examination of the surfaces of C-ring specimens after testing for three months in boiling J-13 and ten-times-concentrated J-13 groundwater, and in the steam phase above these solutions showed that no macroscopic stress corrosion cracking had occurred. To assure that cracks were not present in areas adjacent to the V-notch, specimens of Type 304L sensitized stainless steel, tested in steam as well as the liquid phase, were sectioned through the notch and polished. Examination of these sections under optical and scanning electron microscopes confirmed that no cracks were present.

The 6-month C-ring tests in J-13 and ten-times-concentrated J-13 groundwater have been recently completed. A preliminary examination of the specimens from these tests also shows that no macroscopic cracking had occurred but a small crack nucleus in a Type 316 stainless steel specimen was seen after exposure in the steam phase. Also, in these tests, some pieces of crushed tuff were found to be attached to the surfaces of some specimens tested in the steam phase, presumably due to the deposition of salts at and around the contact areas. Deposition of salts in the three-month tests was not sufficient to cause a similar attachment. A detailed study of the specimens is currently underway.

All C-ring specimens tested in solution have a coating of salt and corrosion scale, whereas stainless steel specimens in the steam phase show patches of unreacted metal surrounded by a brown, rust-colored scale. An attempt was made to examine the surface film which strongly adhers to the base metal using a scanning electron microscope. Unfortunately, the film on the 3-month test specimens was too thin to be resolved by the electron microprobe (excitation potentials as low as 10kV were used). The line and area scans for major elements did not show a film composition different from that of the base metal, although there were some signs of lower chromium concentration in the film. The film also could not be characterized unambiguously when examined in cross-section. A similar examination is now planned on the 6-month test specimens for which the film is expected to be thicker. In contrast to the stainless steels, Incoloy specimens in steam do not show any corrosion scale.

In some areas on the surfaces of 3-month test specimens exposed to the liquid phase, black spots which appeared to be shallow pits under an optical microscope were observed. But under the SEM/microprobe these were determined to be a thin growth of some compound predominantly containing calcium and sulfur, with no indication of pits in the metal (see Fig. 5.1).

Figure 5.1 An SEM micrograph of the surface of a sensitized Type 304L stainless steel specimen showing black spots. The specimen was exposed to "J-13 groundwater" for three months. (x1000)

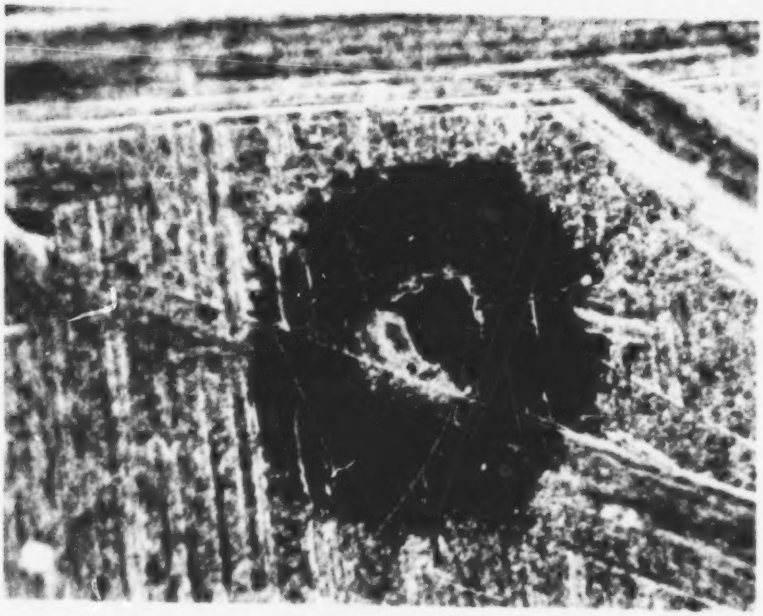

Figure 5.2 Optical micrograph of the surface of a sensitized Type 316L stainless steel specimen tested in "ten-times concentrated J-13" water for three months. The dark circle shows the area from where a salt layer has been removed mechanically. The boundary inside the circle corresponds to the area where a deposit predominantly containing Si, Ca, Aℓ was present. (x500)

On the surface of specimens tested in "ten times concentrated J-13" water small deposits were occasionally observed. These deposits could not be removed by the ultrasonic cleaning of specimens for times up to one hour in water. It was suspected that a pit might be present under such deposits; so they were scraped away with a sharp needle and the area below was examined using optical and scanning electron microscopes. Figure 5.2 shows an optical micrograph of one such area. In this case the deposit was present at the center of the black circular area. The boundary, and a small part of the deposit, are still seen. Microprobe analysis of the deposits suggests that they consist predominantly of Si and small amounts of Aℓ, Ca, K and Cl. During scraping, the thin uniform film of salt was also removed thus exposing the black (metallic) area. Note that both the optical and corresponding SEM photograph (Fig. 5.3) do not show pitting in the metal. However, it is still possible that pits may develop at longer test times.

Figure 5.3 SEM micrograph of the same area as shown in Figure 5.2. (x1000)

It was reported earlier that a few days after starting each test, small amounts of a white solid appeared on some of the tuff pieces near the top of the vessel. A typical micrograph of the white compound is shown in Figure 5.4. An electron diffraction pattern of this compound shows diffuse rings typical of an amorphous solid, and silicon is the only element identified by the microprobe analyses. Therefore, it is inferred that the white compound is amorphous silica which is transported via the vapor phase to cooler areas of the test vessel. Considering the presence of large amount of SiO_2 in solution, as well as in tuff, the precipitation of amorphous silica is reasonable. Silica may also have entered the solution from the Pyrex test vessel which showed leached areas at the end of each test.

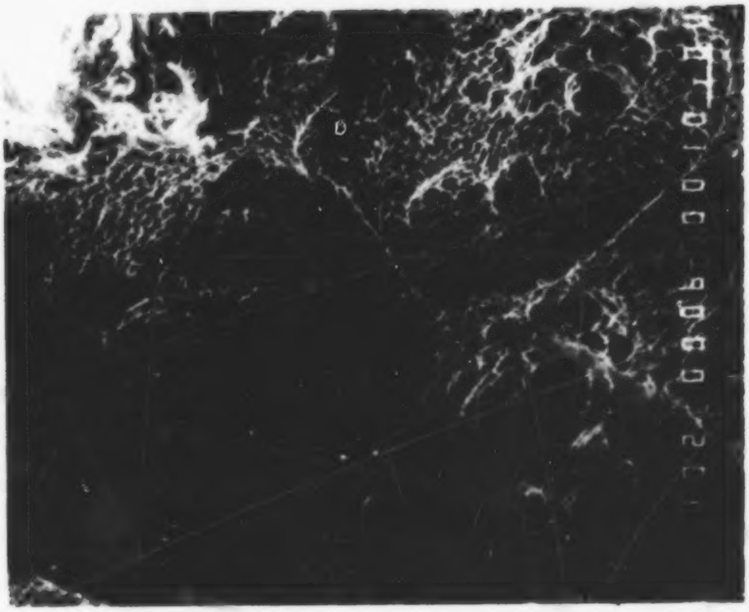

Figure 5.4 An SEM micrograph of the white compound found on the inside of the lid of the test vessel. (x1000)

5.3.2 Water Chemistry Measurements

Preliminary information on the chemical composition of the 3-month test solutions was given earlier; Table 5.3 includes the results of the complete analysis. Results for both tests show that dilution by a factor of two

Table 5.3 Chemical composition of test solutions obtained at the end of three-month tests (μg/mL).

	Reference J-13 Groundwater	Starting Solution: Synthetic J-13 Water		Starting Solution: Ten-Times Concentrated J-13 Water		
		Sample No. 7 (Undiluted, Filtered)	Sample No. 6 (Diluted, Filtered)	Sample No. 10 (Undiluted, Filtered)	Sample No. 9 (Diluted, Filtered)	Sample No. 11 (Undiluted Unfiltered)
Na^+	51	---*	---	867	420	960
K^+	4.9	238	113	244	115	255
Mg^{2+}	2.1	<0.05	<0.05	<0.05	<0.05	<0.05
Ca^{2+}	14	308	151	301	51	332
Fe		<0.1	<0.1	<0.1	<0.1	<0.1
Ni		<0.1	<0.1	<0.1	<0.1	<0.1
Sr^{2+}		3.35	1.97	4.38	2.18	4.24
Al^{3+}		<2.0	<2.0	<2.0	<2.0	<2.0
Cu^{2+}		<0.1	<0.1	<0.1	<0.1	<0.1
F^-	2 2	12.1	7.1	14	8.9	15
Cl^-	7.5	130	72	330	160	330
SO_4^{2-}	22	820	420	1300	660	1300
PO_4^{3-}	0.12	<1	<1	<1	<1	<1
SiO_2	61	414	219	408	205	421
HCO_3^-	120	---	---	---	---	---
NO_3^-	5.6	460	234	---	---	---

*Not determined.

reduces the concentration, within experimental uncertainty, by a factor of two (compare Sample No. 7 with No. 6, and Sample No. 10 with No. 9). Therefore, no significant precipitation appears to occur during the cooling of undiluted solutions. Furthermore, the concentration of various species in filtered (Sample No. 10) and unfiltered (Sample No. 11) solutions is the same within experimental error, which suggests that there was no appreciable amount of suspended solid material which could not pass through Whatman 42 paper.

The results of the chemical analysis of solutions obtained at the end of the 6-month tests are given in Table 5.4. These solutions after filtering at room temperature were analyzed only for those species which showed observable

Table 5.4 Chemical composition of test solutions obtained at the end of six-month tests (μg/mL).

	Starting Solution: Synthetic J-13 Water		Starting Solution: Ten-times Concentrated J-13 Water	
	Sample No. 15 Undiluted	Sample No. 14 Diluted	Sample No. 13 Undiluted	Sample No. 12 Diluted
Na^+	464	217	738	338
K^+	244	113	214	97.1
Ca^{2+}	161	68.5	164	67.5
Sr^{2+}	0.43	0.19	0.45	<0.1
F^-	4	3	5	3
Cl^-	236	111	211	106
NO_3^-	750	354	522	248
SO_4^{2-}	552	282	1260	556
SiO_2	451	210	488	267

concentrations in the 3-month test solutions (see Table 5.3). Once again, the concentration of various species in undiluted solutions (Sample No. 15 or 13) is, within experimental uncertainty, twice the concentration in solutions diluted by a factor of two (Sample No. 14 and 12, respectively), thus suggesting insignificant precipitation during cooling from ≈100°C to room temperature. However, from the following argument it appears that colloids are formed during cooling, which can freely pass through the filter paper. Consider, for example, the concentration of SiO_2 in different test solutions which is ≈450 μg/mL irrespective of the composition of the starting solution (see Tables 5.3 and 5.4). This implies that at the test temperature the solutions are saturated in SiO_2 and, therefore, supersaturated with SiO_2 when the temperature is lowered. But the comparison of the chemical analyses for the normal-concentration and diluted solutions does not indicate that precipitation occurs.

This suggests the formation of colloids on cooling, which are suspended in solution but are sufficiently small in size to freely pass through the filter paper. We have not attempted to characterize the nature of colloids, but a similar argument applies to other species for which solubility decreases with temperature.

It is interesting to compare the 3-month and 6-month test results in Tables 5.3 and 5.4 to determine any changes in water chemistry with time. Among the major ionic species, we note that the concentration of Ca^{2+}, Sr^{2+}, F^- and SO_4^{2-} in solution has decreased with time, possibly due to the conversion of colloids into precipitates. The concentrations of Cl^- and NO_3^- ions also show a change with time, but the direction of change depends on the composition of the starting solution, e.g. the chloride ion concentration increased with time when the starting solution was J-13 groundwater, but decreased when the starting solution was ten-times concentrated J-13 water. In any case the concentration of Cl^-, which enhances the corrosion of many metals, is much higher in the test solutions than in the reference J-13 groundwater.

The exploratory test to determine the possible range of compositions of repository groundwater was continued. In this test a vessel similar to the ones used in the C-ring tests was filled with crushed tuff (0.165 to 0.187 inch size) and distilled water, and then maintained under boiling water conditions. The chemical analysis of the solution obtained at the end of one-month period is given in the third column of Table 5.5. After the one-month test, the solution was drained from and 1150 mL of fresh distilled water was added to the vessel. After the system had been kept under boiling water conditions for another one month, an aliquot of the test solution was collected and analysed. The chemical composition is given in the fourth column of Table 5.5. Once again, after the test, the existing solution was drained from and fresh 1000 mL distilled water was added to the vessel. This time the system was maintained under boiling water conditions for seven weeks before collecting 50 mL of the test solution for chemical analysis; the remaining system is being currently maintained under the boiling water conditions. The analysis of solution which was reacted with crushed tuff for seven weeks is given in the last column of Table 5.5.

A comparison of the chemical analyses of the three solutions successively reacted with crushed tuff shows that the concentration of all cations (Na^+, K^+ and Ca^{2+}) and Cl^-, F^- and NO_3^- ions decreased each time the solution was replaced by distilled water. This suggests that there is only a limited source of these ions in the crushed Topopah tuff. The solubility of compounds containing these ions should be sufficiently high such that a fairly large fraction of the compounds is dissolved during the first reaction period. When fresh distilled water is substituted for the test solution, a large fraction of these ions is removed from the system. The concentration of SO_4^{2-} ions does not show a monotonic change perhaps due to complex interdependence of solubility of this ion on the presence of the other ions. In contrast to the behavior of all ions (except SO_4^{2-}) the concentration of silica in solution increases in successive test solutions. Therefore, the concentration of silica appears to be limited by solubility considerations but not its availability. The fact that the concentration of SiO_2 is higher in the 7-week test solution than in the 1-month test solutions suggests that the dissolution of SiO_2 is either a kinetically slow process or the solubility of SiO_2 depends on the presence of other ions. On the other hand, a higher SiO_2 concentration in the second 1-month test solution (Sample No. 4 in Table 5.5) than in the first 1-month test solution (Sample No. 2 in Table 5.5), suggests that the solubility and perhaps also the dissolution rate of SiO_2 in water is higher when the concentration of other ions is smaller in the solution. Finally, the results in Table 5 indicate that the pH increases in successive test solutions, which correlates well with the concurrent increase in silica concentration.

Table 5.5 Room temperature chemical composition of filtered solutions obtained from the reaction of distilled water with crushed tuff. Composition of reference J-13 groundwater is included for the purpose of comparison (μg/mL).

	J-13 Ground-water	Test Solution Following One-Month Reaction of Crushed Tuff With Distilled Water (Sample No. 2)	Test Solution Following the Subsequent One-Month Reaction of the Same Crushed Tuff With Fresh Distilled Water (Sample No. 4)	Test Solution Following the Subsequent Seven-Week Reaction of the Same Crushed Tuff With Fresh Distilled Water (Sample No. 16)
Na^+	45	308	190	42
K^+	4.9	50.5	21	2.0
Mg^+	2.1	Not determined	<0.1	Not determined
Ca^{2+}	14	930	298	122
F^-	2.2	8.5	<4	2
Cl^-	7.5	160	43.7	23.2
HCO_3^-	120	Not determined	Not determined	Not determined
SO_4^{2-}	22	343	530	247
NO_3^-	5.6	460	188	54
PO_4^{3-}	0.12	Not determined	Not detected	Not determined
Silica	61	95.1	142	214
pH (at room temperature	8.5	8.4	8.5 7.6 (at 100°C)	9.0 8.5 (at 101°C)

5.4 Summary

The stress corrosion cracking susceptibility of Types 304L, 316L and 321 stainless steels, and Incoloy 825 is being investigated under simulated tuff repository conditions. Triplicate specimens of these alloys were exposed to boiling synthetic J-13 or ten-times-concentrated J-13 water in the presence of crushed tuff, and the steam phase above these solutions for 3- and 6-month periods; the 12-month tests are still continuing. The examination of specimens after the 3-month tests shows that no cracking has occurred; the surfaces of specimens tested in steam showed patches of rust and surfaces of specimens tested in the solution had a thin layer of salt and corrosion products. The 6-month tests have been recently completed. A preliminary examination of the 6-month test specimens shows similar behavior as the 3-month test specimens.

A comparison of the chemical analysis of solutions at the end of 3- and 6-month tests suggests that some of the species are present as colloids which grow in size with time. An exploratory test to determine the possible range of compositions of repository groundwater suggests that the crushed tuff contains highly soluble salts containing Na^+, K^+, Ca^{2+}, Cl^-, F^- and NO_3^- ions. The solubility of sulphates and silica appears to be controlled, at least in part, by the presence of other ions in the solution.

5.5 References

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Russel, E. W. and others, "Selection of Barrier Metals for a Waste Package in Tuff," in Scientific Basis for Nuclear Waste Management, VII, G. L. McVay, editor, North Holland, New York, 1984, p. 763.

UCRL-89988, "Selection of Candidate Canister Materials for High-Level Nuclear Waste Containment in a Tuff Repository," R. C. McCright, H. Weiss, M. C. Juhas and R. W. Logan, Lawrence Livermore National Laboratory, 1983.

APPENDIX A

Index of Tapes Containing WAPPA Transmitted to BNL and NRC

1) Tape transmitted to BNL in June, 1983

FILES	CHARACTERS/RECORD		CHARACTERS/BLOCK
1-24	80	17	1360
25-28	136	10	1360

FILE NAME*	FILE NO.*	UNIT* P339 NAME* SUBMODEL * CONTENTS
WPINDX	1	420--20C-02: SEQUENCE OF WASTE PACKAGE (WAPPA) FILES ON TAPE
MCODES	2	(7)-(LOCAT2)-SYSTEM-COMPREHENSIVE LIST OF DATABASE MATERIALS
GAMMA	3	(10)-(RPROP2)-RADIATION-GAMMA BUILD-UP FACTORS, CROSS-SECTION
ORIGEN2	4	(11)-(RADDAT3)-RADIATION-SOURCE TERM=F(TIME) ETC. FROM ORIGEN
THERMAL	5	(20)-(TPROP3)-THERMAL-TEMP. DEP. PROPS. QUADRATIC COEFFS.
RBT	6	(21)-(REPOST2)-THERMAL-REPOSITORY BOUNDARY TEMPS= F(TIME)
MEK	7	(30)-(FPROP2)-MECHANICAL-MECHANICAL PROPERTIRS DATA
FICP	8	(40)-(CTEMPS2)-CORROSION-FLUID-INDEPENDENT CORR. PROPERTIES
FDCP	9	(41)-(CTMPFL3)-CORROSION-FLUID-DEPENDENT CORROSION PROPS.
CED	10	(42)-(CORENC2)-RADIATION-CORROSION ENHANCEMENT DATA
WFLP	11	(50)-(WFPROP3)-LEACH-WASTE-FORM LEACHING PROPERTIES
BFP	12	(51)-(WBPROP2)-LEACH-BACKFILL POROSITY AND DENSITY
NTP	13	(52)-(WSOLUT3)-LEACH-NUCLIDE TRANSPORT PROPERTIES
IV1	14	(1)-INPUT FOR VERIFICATION (17 BARRIER) TEST CASE
IV2	15	(1)-INPUT FOR VERIFICATION (17 BARRIER) RESTART TEST CASE
IS1	16	(1)-INPUT FOR SAMPLE (SIMPLIFIED) PROBLEM
IS2	17	(1)-INPUT FOR SAMPLE (SIMPLIFIED) RESTART PROBLEM
SYS	18	SYSTEM MODEL SOURCE CODE (QA NUMBER: 420-20C-02)
RAD	19	RADIATION SUB-MODEL SOURCE SUBROUTINES
THML	20	THERMAL SUB-MODEL SOURCE SUBROUTINES
MECH	21	MECHANICAL SUB-MODEL SOURCE SUBROUTINES
CORR	22	CORROSION SUB-MODEL SOURCE SUBROUTINES
LCH	23	LEACH SUB-MODEL SOURCE SUBROUTINES
WAPPA	24	420--20C-02: SINGLE FILE WAPPA SOURCE PROGRAM
OV1	25	OUTPUT FOR VERIFICATION (17 BARRIER) TEST CASE
OV2	26	OUTPUT FOR VERIFICATION (17 BARRIER) RESTART TEST CASE
OS1	27	OUTPUT FOR SAMPLE (SIMPLIFIED) WESTINGHOUSE PROBLEM
OS2	28	OUTPUT FOR SAMPLE (SIMPLIFIED) WESTINGHOUSE RESTART PROBLEM

2) Tape transmitted to NRC in November, 1983

FILES	CHARACTERS/RECORD	CHARACTERS/BLOCK
1-15	90	1360
6-18	136	1360
19	80	1360

FILE NAME	FILE	UNIT	FILE DESCRIPTION
WPINDX	1	420--20C-02:	SEQUENCE OF WASTE PACKAGE (WAPPA) FILES ON TAPE
MCODES	2	(7)-(LOCAT2)	SYSTEM-COMPREHENSIVE LIST OF DATABASE MATERIALS
GAMMA	3	(10)-(RPROP2)	RADIATION-GAMMA BUILD-UP FACTORS, CROSS-SECTION
ORIGEN2	4	(11)-(RADDAT3)	RADIATION-SOURCE TERM=F(TIME) ETC. FROM ORIGEN
THERMAL	5	(12)-(TPROP3)	THERMAL-TEMP.DEP.PROPS. QUADRATIC COEFFS.
RBT	6	(21)-(REPOST2)	THERMAL-REPOSITORY BOUNDARY TEMPS =F(TIME)
MEK	7	(30)-(FPROP2)	MECHANICAL-MECHANICAL PROPERTIRS DATA
FICP	8	(40)-(CTEMPS2)	CORROSION-FLUID-INDEPENDENT CORR PROPERTIES
FDCP	9	(41)-(CTMPFL3)	CORROSION-FLUID-DEPENDENT CORROSION PROPS.
CED	10	(42)-(CORENC2)	RADIATION-CORROSION ENHANCEMENT DATA
WFLP	11	(20)-(WFPROP3)	LEACH-WASTE-FORM LEACHING PROPERTIES
BFP	12	(51)-(WBPROP2)	LEACH-BACKFILL POROSITY AND DENSITY
NTP	13	(52)-(WSOLUT3)	LEACH-NUCLIDE TRANSPORT PROPERTIES
IS1	14	(1)-	INPUT FOR SAMPLE SIMPLIFIED PROBLEM
WAPPA	15	420-20C-02B:	SINGLE FILE WAPPA SOURCE PROGRAM
OS1	16		OUTPUT FOR SAMPLE (SIMPLIFIED) WESTINGHOUSE PROBLEM
WAPPA	17		DIFFERENCE FILE CDC VERSION VS. VAX VERSION
WAPPA	18		DIFFERENCE FILE OLD INTERA VERSION VS.NEW INTERA VERSION
CDC JCL	19		JOB STREAM FOR THE CDC COMPUTER

APPENDIX B

List of Potentially Important Differences Between the Revised BNL and NRC Versions of WAPPA

As mentioned in the text there were roughly one hundred statements that contained at least minor variations between the BNL and NRC versions of WAPPA. The majority of these differences will not alter the calculations performed in WAPPA and involve cosmetic changes to the code such as changing output format statements, placing more blank spaces in common statements, placing common blocks in subroutines where the contents of the common blocks are not used, redimensioning arrays, and printing out the wrong quality control identifier.

Examples of these differences include:

- Placing the common block /STHERM/ which contains temperatures in several subroutines for example, RMODEL, INIT, RECHO, and OUTPT. The variables in /STHERM/ are unused in these subroutines and this common block is not found in these subroutines in the BNL version of WAPPA. As far as consistency between the two versions, this is an error of omission as the letter form update did not contain instructors to place /STHERM/ in these subroutines.

- In the NRC version of WAPPA the array TITLE is dimensioned as 20 by 5 whereas in the BNL version it has dimensions of 8 by 5. Again this is an error of omission.

- In the NRC version of WAPPA in the subroutine CINQA the variable QACIN is initialized in data statement as 420--20C-02B, however, it is printed as 420-20C-02A. In the BNL version 420--20C-02B appears in both places. This discrepancy is probably an error in the NRC version of the code.

Differences in the two codes that have the potential to change the predictions of WAPPA include changes in data initialization, logical decision statements, and arithmatic statements.

There were two instances where initial data was changed.

- In the subroutine DATAIN the variable IR3 appeared in a data statement and was set to 14 in the NRC version and 12 in the BNL version. There is no explanation for the difference.

- In the subroutine RADIA the array GFLUX appeared in a data statement in each version as:

```
NRC:  GFLUX/ 1.0E05, 1.0E07, 1.0E09, 1.0E10/
BNL:  GFLUX/ 1.E05,  2.E07,  3.E09,  4.E10/
```

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There was one case where a logical statement differed in the BNL and NRC versions of WAPPA: The following statement appeared in the subroutine DATAIN,

```
NRC:  IF (ICODE.LT.300  or  ICODE.GT.400) GO TO 3
BNL:                             .GE.
```

This statement was changed through the letter update and may be an example of an error in transmission.

Discrepancies in mathematical statements are as follows:

1) Subroutine: DATAIN

```
NRC:  If (ITHIS.EQ.IC2.OR.ITHIS.EQ.IS3) LSKIP=LSKIP * NFLUID
BNL:                                                +
```

The BNL version also required the additional statement

```
BNL:  If (ITHIS.EQ.IC2.OR.ITHIS.EQ.IS3) LSKIP=LSKIP - 1
```

This is probably an error in transmission.

2) Subroutine: DRIVER

The NRC version has the following two statements that do not appear in the BNL version.

```
   DO 4 I = 1, ISNANN
 4 STEMP (I) = SBTMP (1)
```

This discrepancy is an error of omission.

3) In subroutine RADIOL a group of five statements appears in a different segment of the subroutine. It is not clear which version is correct or the influence of moving these statements. The statements are:

```
    CALL RADINT (SGAMFL, RGAMDO, RLEDAT, SLEFR)
    IF(IERCNT. EQ. 0) GO TO 40
    IF (ISEROR (1,IERCNT) .GE. 1000) RETURN
 40 CONTINUE
    IF(IDIAG   .GE. 1) WRITE (ISDG, 1020) SLEFR
```

In the NRC version these statements appear after a check is made of which materials are metal, in the BNL version they appear before the check.

4) Subroutine: RADINT

```
NRC:  IF (FLUX.LT.GFLUX (1)) P=1+FLUX* (ARRAY (JM1,K)-1)/GFLUX(1)
```

This statement does not appear in the BNL version and is a discrepancy of ommission.

5) Subroutine: TTEMP

```
NRC:  DL= (SHTWP/DRM) ** (-0.111)
BNL:                      +
```

This is an error in translation. Review of the letter form update indicated the minus sign was correct.

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3201, 3202

U.S. NUCLEAR REGULATORY COMMISSION

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Several studies were completed this period to evaluate experimental and analytical methodologies being used in the DOE waste package program. The first involves a determination of the relevance of the test conditions being used by DOE to characterize waste package component behavior in a salt repository system. Another study focuses on the testing conditions and procedures used to measure radionuclide solubility and colloid formation in repository groundwaters. An attempt was also made to evaluate the adequacy of selected waste package performance codes. However, the latter work was limited by an inability to obtain several codes from DOE. Nevertheless, it was possible to comment briefly on the structures and intents of the codes based on publications in the open literature. The final study involved an experimental program to determine the likelihood of stress-corrosion cracking of austenitic stainless steels and Incoloy 825 in simulated tuff repository environments. Tests for six-month exposure periods in water and air-steam conditions are described.

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